SULPHUR DISTRIBUTION BETWEEN MOLTEN IRON AND $CaO-MgO-Al_2O_3-SiO_2$ SLAGS CONTAINING FERROUS OXIDE.

SUMMARY.

Although true lime activity values are available from gas/slag sulphur partition in lime-alumina, lime-silica and, to a certain extent lime-alumina-silica melts saturated with calcium sulphide, no attempt has been made to assess true lime activity by slag/metal equilibrium studies on sulphur partition. The first aim of the present investigation was, therefore, to assess the true lime activity in calcium sulphide saturated melts making use of calcium sulphide crucibles whereby the activity of calcium sulphide can be taken as unity simplifying the problem. Calcium sulphide crucibles have been slip-cast successfully for this purpose using absolute ethanol, but it is unfortunate that this project met with little success owing to the poor performance of these crucibles during melts. In the second part of this work, attention was therefore focused on FeO and magnesia crucibles were used. Using these crucibles, the following conclusions have been reached on slag/metal sulphur partition between lime-alumina, lime-alumina-silica or to a certain exte lime-silica melts containing magnesia and ferrous oxide, and pure molten iron at 1550°C.

(1) Magnesia crucibles offered greater advantage than carbon crucibles in view of the fast approach to definite equilibrium and greater accuracy of the distribution ratio (%S)/[%S].

(2) The ability to vary the oxygen potential of the system as desired allowed data to be obtained for the a_{FeO} in low concentration in slags containing CaO, Al_2O_3, SiO_2, and MgO.

(3) The effect of basicity and small amounts of ferrous oxide in the slag on sulphur partition has been studied using the basicity ratio,

$$B = \frac{N_{CaO} + N_{MgO}/2}{N_{SiO_2} + N_{Al_2O_3}} = \frac{(\%CaO) + 0.7(\%MgO)}{0.94(\%SiO_2) + 0.18(\%Al_2O_3}$$

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devised by Bell et.al, which is equally satisfactory as the excess base expression of Hatch and Chipman.

(4) It has been found possible to compute the activity of ferrous oxide in the slag combining the sulphide capacity data from gas/slag work and other thermodynamic data applying the necessary temperature correction for sulphide capacity C_s. The ferrous oxide activity is then given by -

$$a_{FeO} = \frac{44.15 \times C_s}{(\%S)/[a_S]}$$

The derived activity values have been found to be approximat equal to the mole fraction of ferrous oxide calculated from slag analysis over the range of compositions investigated he

(5) Attempts have been made to study the variation of saturation sulphur solubility in the slag with composition using approximate assumptions. In line with the observations of Taylor & Gibbons, and McCaffery & Oesterle, the $(\%S)_{sat}$ decreased with basicity in lime-alumina and lime-alumina-sil slags.

(6) It is interesting that calculations made on the assumption of the existance of $Al_2O_4^{-2}$ ion in the slag fits in reasonably well the activity-ionic fraction product relationship for ferrous oxide in line with Temkin's concept The agreement between Temkin's law and Raoult's law has also been indicated by Chipman and Chang for higher concentrations of ferrous oxide.

(7) In an attempt to apply Flood's theory to the present results the nature of the existance of the aluminate ion in lime-alumina and lime-alumina-silica slags has been pointed out. A dissociation scheme for aluminate ion has been proposed to fit in the observations.

(8) The comparison of the present results to data from two blast furnace plants using the very useful form of plot, FIG.16A, showed that equilibrium is not attained in practice. Suggestion for further work could be the accumulation of sulphide capacity data of simple and more complex slags by reversing the above procedure used to obtain the ferrous oxide activity.

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C O N T E N T S

CHAPTER I

INTRODUCTION

INTRODUCTION

During the last four decades, the application of the laws of physical chemistry has led to a sounder understanding of the principles underlying the processes of iron and steel manufacture. These were formerly carried out purely on an empirical basis by experience.

While the blast furnace process essentially consists of reduction and the steel making is one of oxidation, impurities like phosphorus and sulphur are picked up in the final product from the burden and furnace gases. The detrimental effects of these constituents are very well known. One obvious answer to this problem is to use good raw materials, as it is often said that the quality of the product is governed by the quality of the raw materials used. In view of the depletion of quality raw materials, especially coke, the problem of sulphur removal, however, has become increasingly important in recent years.

Desulphurization is, indeed, a very complicated process, moreover, it is expensive. While the plant data show that equilibrium conditions with respect to sulphur are nearly approached under steel making conditions, this is not so in the blast furnace. This is reflected in lower sulphur distribution coefficients (i.e. $\frac{(S)}{[S]}$ which is a measure of desulphurization) under conditions prevailing in the

blast furnace compared with similar conditions in the laboratory (viz., a third to half of the laboratory equilibrium value). Yet the sulphur distribution coefficients obtained under blast furnace conditions are about 25 to 50 times of those obtainable under open hearth conditions. Part of this difference can be accounted for by the higher concentration of solute elements present in the blast furnace metal and their effect on the activity coefficient of sulphur. The ratios obtained in the electric arc furnace, during the reducing period are intermediate between those obtained in the blast furnace and open hearth furnace. While the sulphur pick up by the metal from the gas atmosphere is very serious indeed in the open hearth process during the melt down period, it is not so harmful in the blast furnace, in the tuyere zone, where tiny droplets of iron are exposed directly to the gas.

The problem is made more complex by the simultaneous existence of three phases - metal, slag and gas, or more precisely four, if the furnace wall is also taken into consideration. A fundamental analysis of the sulphur problem therefore appears rather essential and this could be carried out only through laboratory studies. This could be done by splitting it into slag/metal, slag/gas and gas/metal investigations. There are again two different approaches to each of these, namely, study of the thermodynamics of the reactions involved and secondly study of their kinetics. While the thermodynamic data give an idea about how far the equilibrium conditions are approached in practice, the kinetic considerations

relate equilibrium conditions to time. The latter approach is more difficult for two reasons, namely, the difficulty of making a measurement and secondly the limited application in practice in view of the large number of variables involved. The present investigation, however, is restricted to equilibrium studies of the partition of sulphur between slag and pure molten iron at 1550°C.

Of the three equilibrium studies mentioned above, the gas/metal investigation has thrown light on the activity of sulphur in the liquid metal and how it is affected by the presence of other solutes. Increased activity coefficient of sulphur in the metal would mean increase in chemical potential of sulphur thereby facilitating its flow from metal to slag or gas. This is accomplished by elements like carbon, silicon, aluminium and phosphorus whereas copper, manganese and sulphur have the opposite effect. The slag/gas studies, on the other hand, have given information about the desulphurising power of the slag in terms of such concepts as the "sulphide capacity" of the slag and the "sulphurising potential" of the gas phase. These two quantities are, of course, interrelated. In order that the slag has good desulphurising power, it should hold large quantities of sulphur at a very low chemical potential. This means low activity coefficient of sulphide ions in the slag.

Although the importance of lime in effecting desulphurisation has long been recognised, it was Usann[1] who first put forward the equation for sulphur removal as:-

$$\underline{FeS} + (CaO) \rightleftharpoons (CaS) + (FeO)$$

This implies that high lime and low iron oxide are essential for sulphur removal. Our present knowledge of the mechanism of desulphurization does not differ very much from this fundamental equation. Essentially it is the transfer of sulphur from metal to slag by a reduction mechanism.

i.e. $\underline{S}^{*} + 2e^{-} \rightleftharpoons (S^{--})$

Any factor which can increase the efficiency of this process is one of oxidation i.e. liberation of electrons and this is accomplished by the simultaneous transfer of oxygen from slag to metal as,

$(O^{--}) \rightleftharpoons \underline{O} + 2e^{-}$

Other anodic reactions also accompany the above reaction and these are discussed later. This equation implies that high oxide ion activity in the slag and low oxygen activity in the metal are necessary for removal of sulphur. The former is achieved by high slag basicity. Low metal oxygen activity is obtained by low iron oxide content of the slag or low oxygen potential of the system. This is also obtainable by the use of deoxidants. Reducing conditions which favour low oxygen potential prevail in the blast furnace or electric arc furnace during the reducing period.

Slag/metal equilibrium studies of sulphur offer a direct

* square bracket or underline represent component in liquid metal phase, round brackets refers to component in slag phase.

means of evaluating the lime activities in the slag. However, it is unfortunate that the true lime activities have not been arrived at by distribution measurements. This is due to the difficulty with regard to finding a suitable crucible and, further, lack of information about the variation of activity coefficient of calcium sulphide with slag composition. Hence as a first part of the present investigation, it was intended to study slag/metal sulphur distribution using calcium sulphide crucibles. The slag in this case could be saturated with calcium sulphide, i.e. unit activity, thereby simplifying the problem. This project met with little success and research was made to investigating sulphur partition using magnesia crucibles. This study has thrown light on the activity of 'ferrous oxide' in the slag. Attempts have been made finally to apply the theories of Tankin and Flood to the present results. These have given information about the constitution of lime/alumina slags of which little is known.

CHAPTER II

REVIEW OF LITERATURE

REVIEW OF LITERATURE

The factors governing the equilibrium sulphur partition between liquid slag and iron are fairly well understood at present owing to the large number of publications in this field. The control of sulphur during iron and steel making is governed by its partition between slag and metal, slag and gas, and to a certain extent, gas and metal phases. Moreover, in terms of the interaction of the solute elements in liquid iron and the activities of the constituents of the liquid slag, the gas/metal and slag/gas equilibria have thrown more light on the slag/metal distribution of sulphur. It is therefore proposed to classify the literature under the following headings and review the most significant contributions in detail:-

(1) sulphur in the metal (i.e., gas/metal investigations)

(2) sulphur in the slag (i.e., gas/slag work)

(3) slag/metal distribution of sulphur.

(1) Gas-Metal Investigations

Earlier efforts to understand the behaviour of sulphur in iron have taken two courses:-

(a) to subject the molten iron to an atmosphere consisting of hydrogen and hydrogen sulphide till equilibrium is attained.

or (b) to expose the molten metal to gases containing

sulphur dioxide until equilibrium is established.

The first method has been used by many investigators[2,7,8] and the latter by Maurer and Bischof[9], and Carter and Tahir[9].

The thermodynamics of dilute solutions of sulphur in liquid iron are well known and the effects of the various alloying elements on the activity of sulphur have been established. This has been investigated using the first method via the gas/metal reaction.

$$H_2(g) + [S] = H_2S(g) \quad \ldots\ldots\ldots\ldots\ldots \quad (1)$$

The data for the "equilibrium constant" of this reaction obtained in early investigations[2,3] was not very reliable because of the pick up of sulphur by the crucible material from the gas atmosphere and/or from errors due to thermal diffusion in the gas mixture. Thus Maurer and Bischof[9] estimated an equilibrium ratio

$$K_1 = \frac{p_{H_2S}}{p_{H_2} \cdot [\%S]}$$

for the above reaction which was 100 times that of Chipman and Te Li[9]. However, the former workers observed a linear relationship between the ratio of the partial pressures of hydrogen sulphide and hydrogen, and the sulphur content of the metal which varied from 0 to 20.6%. They did not reach equilibrium as their crucibles (Beryllia) were not resistant to chemical attack by the reacting substances for

more than an hour. The discrepancy in the results was explained by Chipman and Fu Li in the light of the pick up of sulphur by the beryllia crucibles used by Maurer and Bischof and not taking into consideration thermal diffusion. In order to avoid any errors occasioned by thermal diffusion, Chipman and Fu Li preheated the entering gas mixture by molybdenum filaments maintained approximately at the experimental temperature. They used beryllia, magnesia, porcelain and silica crucibles for their work. Of these silica crucibles were better from the point of view of resisting sulphur absorption from the gas mixture.

Chipman and Fu Li obtained a value of 0·09405 at 1600°C for the equilibrium ratio K_S', investigating the above equilibrium between 1595 and 1600°C, and for sulphur contents up to 1·27%. Their results indicated proportionality between sulphur concentration and the ratio of partial pressures of hydrogen sulphide and hydrogen up to at least 1·2%. Because of the difference between the values of the earlier workers[a,c], White and Skalley[b] repeated the same experiments taking special precautions to avoid thermal diffusion. This consisted of using a small reaction chamber maintained at uniform temperature and entirely in the hot zone of the furnace. Their equilibrium ratio was half that of Chipman and Fu Li, viz., 0·0025 at 1600°C. This revealed the thermal diffusion error in the experiments of Maurer and Bischof. The disagreement in results

of Chipman and Fa Li, and White and Skolley was, in part, explicable by the pick up of silicon from the impure alundum containers in the latter's work (ca 2.5%). The latter work of Morris and Williams[6] showed that silicon increased the activity coefficient of sulphur in liquid iron.

Morris and Williams obtained a value of 0.00256 for the equilibrium ratio K_1' at 1615°C, assuming a standard state of 1% sulphur in the metal. Even after correction for the effect of silicon in the metal the value of K_1' of White and Skolley was lower than that of Chipman and Fa Li.

Thus the effect of solute elements on the activity of sulphur in iron was realised and investigations were carried out in this line. Kitchener, Boocock and Liberman[6] studied the influence of carbon on the activity of sulphur in liquid iron using a horizontal molybdenum furnace and taking special care against segregation of sulphur and thermal diffusion of the gases. Segregation difficulties were obviated by analysis of the whole bead of melt contained in a small reaction chamber (a small cavity made of graphite) and thermal diffusion was eliminated by maintaining the chamber at uniform temperature and by a fast stream of the gas-mixture. Equilibrium was attained after one hour which was shorter than the equilibrium times used by Chipman and Fa Li (10 hours) and White and Skolley (6.1/2 hours). Their

results indicated that in a carbon saturated melt the activity of sulphur is doubled at 1560°C. and this is in agreement with their indirect estimate from the work of Meyer and Schulte[10] on the two phase equilibria in the Fe-FeS-MnS system for melts with and without carbon.

Kitchener et al[6] put forward the explanation that silicon and carbon formed a compound with iron in the melt, thus reducing the mole fraction of "free iron" and thereby increasing the activity of sulphur.

Morris and Buehl[7] studied the effect of temperature and the influence of carbon and silicon on the activity coefficient of sulphur. The effect of temperature on the reaction (1)b was small. Their results indicated that on a weight percent basis, carbon had a greater influence than silicon in increasing the activity coefficient of sulphur while the reverse was true on a mol percent basis (1% sulphur was taken as the standard state). At 1600°C and 2.3% carbon in the metal, the activity coefficient was twice that for sulphur dissolved in pure iron, and at carbon saturation, it was more than six times as great. This activity coefficient was greater than that found by Kitchener et al. At 4.35 % carbon the equilibrium ratio for the reaction

$$[S]_{(\text{in Fe - C alloy})} + H_2(g) = H_2S(g) \quad \ldots\ldots\ldots \quad (1)b$$

was expressed by the relation,

$$\log K_1'(b) = -\frac{450}{T} - 1.74$$

In their experiments, thermal diffusion was avoided by conducting the gas mixture at high velocity through a small bore alumina tube directly into the metal contained in graphite or sintered alumina crucibles. The main trouble was aluminium contamination which occurred due to the reaction of carbon in the melt with the alumina crucible and the bubbling and sampling tubes. This also led to loss of carbon from the melt and was circumvented by adding graphite to the melt at short regular intervals.

In the discussion of this paper, Darken[11] has explained the increase of activity coefficient of sulphur by carbon being due to the greater affinity of iron for carbon than for sulphur in a solution containing iron, carbon and sulphur. Assuming that each carbon atom is surrounded by six iron atoms at low concentrations, he was able to calculate 6% increase of activity coefficient of sulphur for each atomic percent of carbon. This is in good agreement with the observed increase of 6 to 7%.

Sherman, Elvander and Chipman[6] reinvestigated the equilibrium

$$H_2O_{(g)} + [S]_{1\%} = H_2S_{(g)} \quad \ldots\ldots\ldots \quad (3)$$

in the temperature range of 1530 to 1730°C and sulphur concentrations up to 4·0%. The free energy change for the above reaction was established as a function of temperature as:-

$$\Delta G^\circ = + 2040 + 0{\cdot}04T$$

$$\text{and } \log K_1 = -\frac{2130}{T} - 1{\cdot}429.$$

From the above data, the free energy of solution for sulphur in iron can be calculated. The free energy change for the reaction

$$1/2S_{2(g)} = [S]_{1\%} \quad \ldots\ldots\ldots\ldots \quad (2)$$

is given by

$$\Delta G^\circ_2 = -31,520 + 5{\cdot}37T$$

Sherman et al[6] found that the ratio K_1' was not a true constant but varied with the sulphur content. The true equilibrium constant was obtained by extrapolating their values to zero sulphur (using infinitely dilute solution of sulphur in iron as the standard state). They used an induction furnace and alip-cast alumina crucibles for their work. Thermal diffusion was avoided by pre-heating of the gas and by adding argon to the gas mixture. Taking the values of f_S^{Si} (for the effect of silicon on the activity coefficient of sulphur) from the work of Morris and Williams[5], they found good agreement among the results of Morris and Williams, White and Skolly[4], Hauser, Hemmx and Nobius[13] and their own.

The k_1' values of Chipman and Fu [3] were higher.

In a later paper, Sherman and Chipman [18] developed the method for computing the overall activity coefficient in a multi-component system. This method was based on the observation of Norris and Buehl [7] on the effect of carbon and silicon on the activity of sulphur. Sherman and Chipman examined the effect of manganese, carbon, phosphorus, sulphur, aluminium, silicon and copper on the activity coefficient of sulphur in molten iron solutions containing these elements. It was found that phosphorus, aluminium, silicon and carbon increased the activity coefficient of sulphur, phosphorus had the least effect, while carbon was most effective. Similarly, copper, manganese and sulphur decreased the activity of sulphur, copper had the least effect and sulphur the greatest. In a multicomponent system, the activity coefficient for low concentrations can be expressed in the form [10, 16]:

$$f_s = f_s^s \cdot f_s^c \cdot f_s^{si} \ldots$$

or $$\log f_s = \log f_s^s + \log f_s^c + \log f_s^{si} + \ldots$$

where

f_s = the overall activity coefficient of sulphur

f_s^s = the activity coefficient of sulphur in the simple binary Fe + S

and f_s^c, f_s^{si}.... are the coefficient representing the effect of carbon, silicon, etc. on the activity of sulphur (interaction coefficients).

For higher concentrations, Chipman[10] proposed a graphical method which, in essence, consists of finding from the log f_s v. % added element plot the amount of solute B which has the same effect on the activity coefficient of sulphur as solute A. This equivalent amount of B is added to the actual percentage of B. The activity coefficient corresponding to this total represents the combined effect of A and B. This process is repeated for the third solute and so on. This method gave better results than the straight summation of logarithm of activity coefficients.

The high temperature experimental data agreed reasonably well with the low temperature studies extrapolated to high temperatures with the aid of heat capacities and heat of formation of substances. Such studies have been carried out by Hollinek and Zakowski[16], and Brinske and Kapustinsky[16] on the reaction of solid iron sulphide with hydrogen at 900°C.

The mechanism whereby sulphur is transferred from sulphur dioxide containing gases to molten iron has been the object of investigation of Maurer and Bischof[9], and Carter and Tahir[9]. The former used gas mixtures containing sulphur dioxide and oxygen while Carter and Tahir used mixtures of sulphur dioxide and nitrogen, and sulphur dioxide, oxygen and nitrogen. Maurer and Bischof found a proportionality between the final sulphur content and the ratio of the partial pressures of sulphur dioxide to oxygen whereas Carter

and Tahir observed no relationship at all. Both Herty et al[17] and, Maurer and Bischof[8] suggested the following reaction.

$$Fe(\ell) + SO_2^{(g)} = FeS(\%\ in\ Fe) + O_2^{(g)} \quad \ldots\ldots\ldots(3)$$

The symbol (% in Fe) signifies that the activity of FeS is equal to its percentage and that its standard state is a one percent solution in liquid iron. The results of Herty et al, Maurer and Bischof and the steel works data of Diehl[82] were explicable by means of reaction (3).

However, Chipman and Fu Li[3] have shown this reaction to be impossible because of its high positive free energy change. The free energy change for the reaction (3), according to Carter[9], is

$$\Delta G^\circ_3 = + 55,000 - 13.99T$$

Therefore the following reaction was suggested by Chipman and Fu Li.

$$3\ Fe(\ell) + SO_{2(g)} = FeS(\%\ in\ Fe) + 2FeO(\%\ in\ Fe) \quad \ldots\ldots(4)$$

for which, the standard free energy change, as given by Carter[9], is

$$\Delta G^\circ_4 = + 1600 - 23.32T.$$

In their work, Carter and Tahir[9] did not reach true equilibrium. The "equilibrium" value of sulphur obtained was really the result of steady state conditions, i.e. the rate at which sulphur entered the metal from the gas phase was equal to the

rate at which sulphur entered the continuously forming oxide phase from the metal. The slag, instead of forming a layer on the surface of the molten metal, moved to the periphery and was absorbed by the magnesia crucible. Thus the metal always appeared to be in contact with the gas.

Because of the presence of sulphur vapour in the exit gases the reaction was formulated in two stages as follows.

$$2\,Fe(l) + SO_2(g) = \underline{2\,FeO} + \tfrac{1}{2}S_2(g) \quad \ldots\ldots \quad (5)$$

$$Fe(l) + \tfrac{1}{2}S_2(g) = \underline{FeS} \quad \ldots\ldots\ldots \quad (6)$$

It can be seen that the summation of reactions (5) and (6) yields the overall reaction (4) of Chipman and Fa Li[0]. The results of Carter and Tahir indicated that about 70 - 75% of sulphur dioxide reacted according to equation (5) and the remainder according to equation (6). No sulphur dioxide was detected in the exit gases. Reactions (5) and (6) were followed by the separation of oxide-rich phase when saturation was reached.

The relationship between sulphur content of the metal, partial pressure of sulphur dioxide, and temperature was given by the relation.

$$\log \frac{[\%S]}{p_{SO_2}} = \frac{2642}{T} + 0.35$$

(2) GAS - SLAG INVESTIGATIONS.

It is only in recent years that gas-slag work has received much attention. There is a wide gap in the literature between the first investigation of Herty et al[17] and the subsequent investigations of Fincham and Richardson[18] and of Carter and Macfarlane[19]. The main reason for this was that data on sulphur containing gases was not reliable enough to make the work worth doing. The main feature of such work is that it enables satisfactory interpretation of results, as the activities of the constituents in the gas-phase could be equated to their partial pressures at high temperatures. Moreover, if a noble metal container is used to hold the slag, little or no contamination from the crucible occurs, introducing fewer complications in the study of binary and ternary systems and reducing analytical difficulties. However, the longer equilibrium time compared with slag-metal work, the "creeping out" of the slag, volatilisation of some of the slag constituents, blowing out of the slag powder by the gas mixture, thermal diffusion in the gas mixture, and the expensive nature of the crucible are all disadvantages.

Herty et al[17] found a direct relationship between the concentration of sulphur dioxide over the molten steel bath and the concentration of sulphur in the slag. This indicated the following

reactions taking place between slag and gas:-

$$SO_2(g) + 3CO(g) + (CaO) = (CaS) + 3CO_2(g) \cdots (7)$$

$$SO_2(g) + (CaO) + 3Fe(l) = (CaS) + 3(FeO) \cdots\cdots (8)$$

Thus sulphur in the slag was assumed to be present almost wholly as calcium sulphide (because CaS is more stable than FeS or MgS). Qualitatively these equations showed that high gas sulphur contents and reducing conditions gave high slag sulphur contents.

The desulphurizing abilities of the constituents in the slag can be satisfactorily interpreted in terms of sulphur and oxygen pressures by equations of the type

$$CaO(s) + \tfrac{1}{2}S_2(g) = CaS(s) + \tfrac{1}{2}O_2(g) \cdots\cdots\cdots (9)$$

with a free energy change of $\Delta G^\circ_9 = 23,020 - 1{\cdot}25\ T$.

The above free energy change can be obtained from the data of Rosenqvist[20] for the reaction.

$$CaO(s) + H_2S(g) = CaS(s) + H_2O(g) \cdots\cdots\cdots (10)$$

along with the free energies of formation of H_2O and H_2S.

Although the necessity for the simultaneous transport of oxygen from gas to slag to "pump out" sulphur from slag to gas has been realised by Richardson and Withers[21], Fincham and Richardson[10] examined this idea in the light of different oxygen pressures.

These workers have shown that a wide range of oxygen pressures, sulphur equilibrium between gas and slag is controlled by the two following reactions operating simultaneously.-

$$O_{(melt)} + \tfrac{1}{2}S_{2(g)} = S_{(melt)} + \tfrac{1}{2}O_{2(g)} \cdots\cdots \quad (11)$$

and

$$O_{(melt)} + \tfrac{3}{2}S_{2(g)} + \tfrac{3}{2}O_{2(g)} = SO_{4(melt)} \cdots\cdots \quad (12)$$

It was shown that reaction (11) is of importance at oxygen pressures less than 10^{-6} atmosphere whereas the latter is predominant at oxygen pressures greater than 10^{-6} atmosphere when the sulphur in the slag is present mainly as sulphate. Reaction (11) is of practical importance.

The equilibrium constants for the two reactions can be expressed in terms of the quantities sulphide (C_S) and sulphate (C_{SO_4}) capacities of the melt respectively by means of the following equations.

$$K_{11} \cdot \frac{(a_{O^{--}})}{(\gamma_{S^{--}})} = \frac{(\%S)\, P_{O_2}^{1/2}}{P_{S_2}^{1/2}} = C_S$$

$$K_{12} \cdot \frac{(a_{O^{--}})}{(\gamma_{SO_4^{--}})} = \frac{(\%SO_4)}{P_{S_2}^{1/2}\, P_{O_2}^{3/2}} = C_{SO_4}$$

Thus for a given sulphur pressure in the gas, the plot of log (% S in the melt) v. P_{O_2} passes through a minimum corresponding to $P_{O_2} = 10^{-6}$ atmosphere. With 2% SO_2 input in the gas, a slag

with the composition 41% CaO, 52% Al_2O_3, and 7% SiO_2 became saturated with calcium sulphide at $p_{O_2} = 10^{-9}$ atmosphere while at $p_{O_2} > 10^{-8.5}$ atmosphere, the formation of pyrosulphate became significant.

The following assumptions were inherent in their work. (a) The substitution of small amounts of sulphur does not alter significantly the activity of replaceable oxygen ions, and (b) for the low concentrations of sulphur encountered, the activities of (S^{-2}) or (SO_4^{-2}) are proportional to the sulphur concentrations. In other words, $\gamma_{S^{-2}}$ or $\gamma_{SO_4^{-2}}$ remains substantially constant.

Their experimental technique consisted of exposing various silicate and aluminate melts held in inert platinum cups to a gas mixture containing H_2, CO_2, SO_2 and N_2.

Fincham and Richardson studied the effect of temperature on the equilibria and the conditions for optimum desulphurization of the metal in the light of gas-slag equilibria. In line with the ΔH° values for the two reactions, increase in temperature increases the amount of sulphur in the melt as sulphide, but decreases the amount of sulphate present. The variation of sulphide capacity with temperature is substantially linear, increase in temperature increasing C_S. The factors leading to efficient desulphurization of metals by slag or high sulphide capacities

are high oxide ion activity, low $\gamma_{S^{-2}}$ value, and favourable free energy of formation of the sulphide from the oxide. Among the binary silicate melts, the sulphide capacities of $FeO.SiO_2$ and $CaO.SiO_2$ are of interest because the former is about 26 times that of the latter at a molar concentration of base of 0.53. The greater sulphide capacities of $FeO.SiO_2$ melts compared with those of $CaO.SiO_2$ melts (containing more than 33 mole % SiO_2) is attributed to the much higher oxide ion activity of the former. However, the nearly equal desulphurizing powers of $FeO.SiO_2$ and $CaO.SiO_2$ melts is due to the higher oxygen activity in the metal in equilibrium with $FeO.SiO_2$ slags.

Some correlation has been achieved between their results and those of Hatch and Chipman[33] when the former are extrapolated to extremely low oxygen pressures, the sulphide capacity values from the results of Hatch and Chipman being calculated from available thermodynamic data. Similarly reasonable agreement has been claimed at higher basicities between the results of Fetters and Chipman[30] and those of Winkler and Chipman[35] compared with an extrapolated C_S curve of Fincham and Richardson. Similarly, the points representing the sulphur content of iron saturated with carbon in equilibrium with $CaO-SiO_2-Al_2O_3$ melts containing 1.5% sulphur (calculated from the results of Fincham and Richardson) agreed fairly well with the metal iso-sulphur lines in the pseudo-ternary diagram $CaO + MgO - Al_2O_3 - SiO_2$ of Hatch and Chipman.

To date, the assessment of the true activities of lime has not been possible due to lack of information about the activity coefficient of calcium sulphide in the slag. This has been circumvented to some extent, in the past, with certain approximations. Thus Carter and Macfarlane[10] carried out investigations on the binary slags of the systems $CaO-Al_2O_3$ and $CaO-SiO_2$ using gas-mixtures containing CO, CO_2 and SO_2 at 1500°C and used their results to determine the activities of lime, and alumina or silica in these melts as follows:-

The equilibrium constant for the reaction,

$$(CaO) + \tfrac{1}{2}S_2 = (CaS) + \tfrac{1}{2}O_2 \qquad \ldots\ldots\ldots \qquad (19)$$

is given by

$$K_{19} = \frac{a_{CaS}}{a_{CaO} \cdot A} \quad \text{where } A = \sqrt{\frac{PS_2}{PO_2}} \text{ ("sulphurising power" of the gas)}$$

Similarly for a standard slag of unit lime activity the relation becomes

$$K_{19} = \frac{a^{\circ}_{CaS}}{A^{\circ}} \quad \text{where the superscript zero refers to the standard slag.}$$

It follows, therefore, from these two relations, that

$$a_{CaO} = \frac{a_{CaS}/A}{a^{\circ}_{CaO}/A^{\circ}} = \frac{\%S/A}{\%S^{\circ}/A^{\circ}}, \text{ substituting weight percentages of sulphur for activities.}$$

The following assumptions were implicit in this procedure:-

(1) For slags sufficiently far removed from sulphide saturation, the activity coefficient of calcium sulphide does not vary significantly with slag composition or sulphur concentration.

(2) The activity of lime is not lowered significantly by the substitution of sulphide for oxide. This should hold good for low concentrations.

(3) No appreciable amount of sulphur is present in the slag as aluminium or silicon sulphide, i.e. linked to aluminium or silicon atoms.

The proportionality between A value and %S in the melt up to 1·6% sulphur suggested that γ_{CaS} was constant. A slag of the composition 60·6% CaO, 32·4% Al_2O_3 and 7% SiO_2 was chosen as the standard slag of unit lime activity. This composition refers to the 1500°C isotherm in the $CaO-Al_2O_3-SiO_2$ system which passes through the primary phase field of CaO (No liquid slag in the $CaO-Al_2O_3$ system is in equilibrium with solid CaO at 1500°C).

The Gibbs-Duhem equation was used to derive the activity of the other component, $a_{Al_2O_3}$ or a_{SiO_2}, in binaries and approximate values obtained for the free energy of formation of binary aluminates and silicate using the activity product principle. Their results indicated that, for the gas-composition investigated, A value decreased with rise of temperature and that γ_{CaS} is greater for $CaO-Al_2O_3$ slags than for $CaO-SiO_2$ slags of the same lime activity (or else the effect of temperature on the solubility of sulphur is unusually large).

The agreement between Carter and Macfarlane[19], Kalyanram et al[20] and Richardson et al[18,26,27] on sulphide capacities is very good but was formerly not so good because of poor data for ΔG^{o} for the formation of sulphur monoxide.

Chipman[28] has calculated the activity of alumina from a_{CaO} values of Carter and Macfarlane[19] using the solubility data of the compounds between CaO and Al_2O_3 and found that this activity curve is different from that calculated using Gibbs-Duhem equation. A correction has therefore been made to log a_{CaO} which increases progressively with the concentration of alumina. The lime activity curves have therefore been redrawn. In the same paper, a comparison has been made among the available slag-metal data by means of a plot of log C_S and log ν_S versus a basicity function R

where $R = \dfrac{\sum N_{CaO}}{N_{SiO_2} + 0.5\, N_{Al_2O_3}}$

$\sum N_{CaO}$ being obtained by treating MgO same as CaO with the molecular weight 56.

Following up the work of Carter and Macfarlane, Hall and Kalyanram[29] investigated the effect of addition of magnesia on the sulphur absorption characteristics of slags composed of binary and ternary mixtures containing CaO, Al_2O_3 and SiO_2 at 1500°C and expressed their lime activity values by the method used by the former. In accordance with the expected poor desulphurising power of magnesia,

their "lime equivalent" (which represents the combined effect of CaO and MgO, and is proportional to activity of oxide ions increased with increase of MgO at constant CaO/SiO_2 or CaO/Al_2O_3, while it decreased with increase of MgO at constant SiO_2 or Al_2O_3 in $CaO-SiO_2$ or $CaO-Al_2O_3$ slags respectively. These results also indicated that in more acid slags the effect of replacing CaO by MgO is very small. Similar investigations on $CaO-Al_2O_3-SiO_2$ slags(plot of "lime equivalent" v. $\frac{CaO}{Al_2O_3 + SiO_2}$ for various MgO contents) suggests an optimum desulphurising power in the region of 15% Al_2O_3 in these slags..

In a subsequent paper[25] Bell et al worked out a correlation between A_{CaO} i.e. $\frac{\gamma_{CaO} \cdot \gamma_{CaS}}{\gamma_{CaS}}$ and the basicity ratio

$$\frac{N_{CaO} + \frac{N_{MgO}}{2}}{N_{SiO_2} + \frac{N_{Al_2O_3}}{3}} = \frac{(\%CaO) + 0{\cdot}7(\%MgO)}{0{\cdot}94(\%SiO_2) + 0{\cdot}28(\%Al_2O_3)}$$

This ratio correlates well with the data of Abraham and Richardson[20]. The agreement between the sulphide capacity values obtained in this work and those of Pincinn and Richardson[10] was good, after correction for free energy of formation of SO has been made.

In the light of the K value of Rosenqvist[20] (490 at 1500°C) for the reaction

$$\underline{S} + CaO_{(s)} + \underline{C} = CaS_{(s)} + CO_{(g)} \quad \ldots\ldots\ldots\ldots \quad (14)$$

and the data of Hatch and Chipman it suggests that their h_{CaO} values are higher than the true c_{CaO} values for the slags. Again, using the data of Hatch and Chipman and the γ_{CaS} (= 4·5) value of Taylor and Stobo[69], the following relation for the slag-metal distribution ratio has been derived.

$$\log \frac{(\%S)}{[\%S]} = 1{\cdot}3 \left[\frac{(\%CaO) + 0{\cdot}7(\%MgO)}{0{\cdot}94(\%SiO_2) + 0{\cdot}16(\%Al_2O_3)} \right] + 0{\cdot}22$$

Abraham, Davies, and Richardson[80] studied the system MnO + SiO_2 at 1500°C and 1650°C and the pseudobinary systems MnO.SiO_2 + CaO.SiO_2 and MgO.SiO_2 + CaO.SiO_2 at similar temperatures. It was shown that in MnO-SiO_2 melts, γ_{MnS} at concentrations up to 2 mol % varied by a factor of three across the range of composition of the liquids. Examination of their data in the light of Flood-Grjotheim[80] equation show that for MgO.SiO_2 + CaO.SiO_2, the sulphide capacities vary linearly across the pseudobinary, while for MnO.SiO_2 + CaO.SiO_2, they deviate by a factor of 30% from this relationship as is seen from the small "hump" in the plot of log C_S v. N_{MnO}. This deviation is attributed to the higher than "ideal" activity coefficients for MnO in the same melts. Their experimental set up and gas-mixtures were the same as those of Fincham and Richardson[16]. In a subsequent investigation, Abraham and Richardson[87] measured the sulphide capacities of various phosphate melts, viz., CaO + P_2O_5, CaO + P_2O_5 + SiO_2 and CaO + P_2O_5 + Al_2O_3 using a gas mixture containing H_2, CO_2 and CO. Their results indicated that P_2O_5

on a mol per mol basis, is much more effective than SiO_2 or Al_2O_3 in lowering sulphide capacities. The correlation between these workers and Hatch and Chipman[20] is nearly satisfactory. The deviation has been explained by the fact that the latter did not always reach equilibrium with respect to the partition of silicon between slag and metal.

It has been seen from the above discussion that the true lime activity values, although of great significance, have only been found approximately. This is because of the inability to assess the activity coefficient of the sulphide ion for each slag composition. As regards the behaviour of γ_{CaS}, the results reported have hitherto been contradictory. For example, while Sharma and Richardson[21] have reported a decrease of γ_{CaS} with increase in mole fraction of lime the reverse has been found by Taylor, Gibbons[22] and Cameron[23].

Taylor and Gibbons[22] studied the systems $CaO-Al_2O_3$ and $CaO-Al_2O_3-SiO_2$ using gas mixtures of $(CO_2 + CO_2 + CO)$ at 1550°C, whereas Sharma and Richardson[21,24] studied the systems $CaO-Al_2O_3$ and $CaO-SiO_2$ using gas mixtures of $(CO_2 + H_2)$ containing sulphur dioxide and H_2 at 1500°C and 1550°C. Both these workers were able to calculate the activity of lime in CaS saturated melts. Taylor and Gibbons have shown excellent agreement between their lime activity data with those of Sharma and Richardson,[31] and those of Ball and Kalyanram[29] by recalculating the data of these workers. This

calculation is based on the assumption that the activity of lime remains constant whereas γ_{CaS} may change slightly with composition. In the light of equation (13) it can be seen that the plot of (% S) in the slag V. A value is a curve if a_{CaO}/γ_{CaS} varies. However, if it is assumed that a_{CaO} remains substantially constant, then the other factor which accounts for the curved plot is the variation of γ_{CaS}. Replotting the sulphide capacity data of Sharma and Richardson[31] and directly the data of Kalyanram and Bell[30] along with their own results, Taylor and Gibbons have shown that γ_{CaS} can be obtained directly from the plot of (%S) V. A value. It is given by the reciprocal of the intercept which the line joining the origin through the point in question makes with the saturation line, i.e. line representing calcium sulphide saturation. In this way new lime activity values have been calculated using these values for activity coefficient of calcium sulphide.

Sulphur equilibria between CaO-FeO slags and gas mixtures containing SO_2 or SO_2 + CO has been the object of investigation of St. Pierre and Chipman[35]. This investigation consisted of determining the partial pressure of oxygen in the gas making use of the ratio j $\left(= \frac{Fe^{+a}}{Fe^{+a} + Fe^{+b}}\right)$ in the FeO slags in equilibrium with the gas mixture. They found that the sulphur content of the slag had no effect on the relationship between the j-ratio and and the calcium content at constant p_{O_2}. In a subsequent investigation

the same workers equilibrated FeO slags with additions of CaO, SiO_2 and MgO with atmospheres of SO_2 containing additions of CO and O_2. The presence of CaO was found necessary for absorption of sulphur as sulphate. They concluded that in lime-iron oxide slags at constant atmospheric conditions, substitution of CaO for FeO slightly decreases sulphide content and greatly increases sulphate content. At constant oxygen and sulphur pressures, the sulphur absorption is nearly independent of the ratio CaO/FeO, but is decreased by the addition of silica or magnesia. These observations are in line with the effect of silica in lowering the oxide ion activity and the effect of magnesia additions in increasing $\gamma_{S^{--}}$. The effect of temperature has also been examined, and found to be the same as the observations of Flinhan and Richardson[10].

(3) SLAG-METAL REACTIONS

The mechanism whereby sulphur is transferred from metal to slag can be written, more usefully, in an ionic form as

$$(O^{--}) + \underline{S} = (S^{--}) + \underline{O} \quad \ldots\ldots\ldots \quad (15)$$

The equilibrium constant for this reaction is given by,

$$K_{15} = \frac{(a_{S^{--}})[a_O]}{[a_S](a_{O^{--}})}$$

Sulphur distribution between slag and iron is usually characterized by the ratio, $(\%S)/[\%S]$. The variables affecting the distribution ratio are therefore the oxygen activity in the metal, the oxide-ion activity in the slag and the activity coefficients of sulphur in the slag and the metal. Most of the work in the past has been aimed at assessing these variables and correlating with the distribution ratio.

Hatch and Chipman[88] have given a brief survey of early literature and the subject under blast furnace and steel making conditions has been critically reviewed[87, 88].

Amongst the pioneers, Holbrook and Joseph[89] measured the relative desulphurising power of blast furnace slags without reference to equilibrium conditions, while Oelsen and Maetz[40] linked the sulphur distribution ratio with silica reduction by means of their

"Kennzahl" i.e., $\frac{(\%S)}{[\%S]} \cdot \frac{1}{[\%O]^{1/2}}$. The work of Bardenheuer and Geller[41], despite criticism[50], marks an era in the history, because their results are accepted even today. This work has been reviewed in detail elsewhere[33].

Bardenheuer and Geller studied sulphur distribution between molten iron and iron-oxide slags with additions of lime, silica, alumina and manganese oxide in magnesia and alumina crucibles using a high frequency induction furnace. Temperature measurements were made using an optical pyrometer and were subject to a fairly large error because of the inaccurate emissivity correction used. The source of sulphur was FeS or CaS added to the slag and equilibrium was thought to have been attained in 10 minutes. The slag and metal were cast into a copper chill mould and analysed.

Their results are summarised in the expressions.

$$\log L_{FeS} = \frac{2200}{T} - 0.714 \quad \text{where} \quad L_{FeS} = \frac{(\%S)}{[\%S]}$$

These results agree well with the later work of Fetters and Chipman[30] and the activity coefficients of FeS in iron as calculated from phase diagram by Chipman[44]. Bardenheuer and Geller concluded that lime was a better desulphuriser than iron-oxide while additions of silica and magnesia together tended to lower the coefficient L_{FeS}.

Darken and Larson[66] used the results of Bardenheuer and Geller[41] to derive the expression

$$\frac{(\%S)}{[\%S]} = N_0 \left\{ 2{\cdot}6 + 1{\cdot}6 \frac{(CaO')}{(FeO)} (L = 2) + 11\,[\%Mn] \right\}$$

by a consideration of the reactions.

$$[FeS] = (FeS) \quad \ldots\ldots\ldots\ldots\ldots \quad (36)$$

$$[FeS] + (CaO) = (CaS) + (FeO) \quad \ldots\ldots\ldots \quad (37)$$

$$[FeS] + [MnO] = (MnS) + (FeO) \quad \ldots\ldots\ldots \quad (38)$$

where,

$L = \frac{CaO - 4\,P_2O_5}{SiO_2}$, $CaO' = CaO - 4P_2O_5$ and N_0 = total number of mols per 100 g of slag.

The calculated sulphur ratios agreed fairly well with the observed ratios of Open-hearth heats. It is easy to see that $L = 2$ corresponds to the stable compound $2CaO.SiO_2$ and no desulphurization by lime occurred when L was less than 2.

A similar equation has been used by Bentrup[20], viz.,

$$\frac{(\%S)}{[\%S]} = \frac{(\%S)_{Fe} + (\%S)_{Ca} + (\%S)_{Mn}}{[\%S]} = k_{FeS} + k_1 \frac{(CaO)}{(FeO)} + k_2[\%Si]$$

where $(\%S)_{Fe}$ represents sulphur in slag present as FeS and so on. His calculations indicated that lime is effective in controlling desulphurization only if silica and iron-oxide are kept low.

Thus the concept of "free base" as a criterion to measure desulphurizing ability was realized and the thirst to understand the mechanism of desulphurization under iron and steel making conditions increased. Correlation of the distribution ratio with some measure of the "free" or "excess" base was attempted. For example, Schenck[27]

introduced the concept of "free concentrations" of (FeO) and (CaO) in the slag for the reaction (17) and found that the "equilibrium constant" varied with the silica content of the slag. The free concentrations were determined from charts relating the dissociation constants of the various slag compounds ($2CaO.SiO_2$, $2FeO.SiO_2$, $3CaO.P_2O_5$ or $4CaO.P_2O_5$ and $2CaO.Fe_2O_3$) with the free concentration of slag components, slag composition and temperature.

Grant and Chipman[40] made a different approach to the mechanism of desulphurisation under Basic Open Hearth conditions. They found that the usual basicity ratios:-

$$V \text{ Ratio} = \frac{\%CaO}{\%SiO_2}$$

$$V' \text{ Ratio (of Körber and Oelsen)} = \frac{\%CaO' \times 100}{\%CaO + \%SiO_2}$$

$$\text{where } \%CaO' = \%CaO - 1{\cdot}18\ (\%P_2O_5)$$

$$B \text{ Ratio (of Herty)} = \%CaO - 0{\cdot}93\ (\%SiO_2) - 1{\cdot}18\ (\%P_2O_5)$$

$$L \text{ Ratio (of Larken and Larson)} = \frac{CaO - 4\ P_2O_5}{SiO_2} \text{ in mols per 100g slag}$$

$$R \text{ Ratio} = \frac{(CaO)}{SiO_2 + 0{\cdot}634P_2O_5} \text{ in mols per 100 g slag}$$

$$B/A \text{ Ratio} = \frac{CaO + MnO}{2SiO_2 + 4P_2O_5} \text{ in mols per 100g slag}$$

did not correlate well with sulphur distribution but that a quantity defined as "excess base" gave a good correlation in the range of compositions studied. Excess base was defined as

Excess Base = $nCaO + nMgO + nMnO - 2n\,SiO_2 - 6nP_2O_5 - 2n\,Al_2O_3 - nFe_2O_3$

where n is the number of mols of oxide per 100 g of slag and is based on the assumption of the compounds $2CaO.SiO_2$, $4CaO.P_2O_5$, etc. in the slag. It is thus some measure of the free oxygen ions. When the distribution ratio was plotted against this function, the data could be described by an "average or standard" line indicating the near equivalency of the basic oxides in their role in desulphurization and the neutral role ("diluent") of FeO. Fluorspar has no effect, as also had temperature in the range 1540 - 1660°C, although higher temperatures appeared to give poorer sulphur partitions. Because the temperature effect was in the opposite direction (desulphurization is endothermic), they discarded the usual mechanism and proposed an alternative mechanism for desulphurization.

$$[FeS] = (FeS) \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (16)$$

$$[MnS] = (MnS) \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (10)$$

i.e. direct partition of the sulphide between slag and metal. Their work, however, was subject to criticism[50,53] because they overlooked the importance of oxygen potential, did not regard 'FeO' as a base and the effect of temperature was difficult to clarify.

Carter,[52] however, tried the various plots.

$(\%S)/[\%S]$ vs $\dfrac{\text{"Excess Base"}}{[\%O]}$

$(\%S)/[\%S]$ vs $\dfrac{n_{O^{--}}}{[\%O]}$

$(\%S)/[\%S]$ vs $\dfrac{\text{"Excess Base" (corrected for dissociation of orthosilicate)} + (FeO)}{[\%O]}$

and K_D vs $(n_{O^{--}})$

where, $K_S = \dfrac{(a_{FeO})(a_{S^{--}})}{[a_{FeS}]}$

and $(n_{O^{--}}) = n_{CaO} + n_{MgO} + n_{MnO} + n_{FeO} - 2n_{SiO_2} - 3n_{P_2O_5} - 3n_{Al_2O_3}$

and arrived at the equation

$$\frac{(\%S)}{[\%S]} = K \frac{\Sigma(n_{MO})}{[\%O]}$$

which gave the best correlation when

$$\Sigma(nMO) = n_{CaO} + n_{MgO} + n_{MnO} + n_{FeO} - 2n_{SiO_2} - 3n_{P_2O_5} - n_{Al_2O_3} - n_{Fe_2O_3}.$$

What this implies is not difficult to see. Desulphurization, for low or high FeO contents, could be explained by the usual mechanism

$$(O^{--}) + [S] = (S^{--}) + [O] \quad \ldots\ldots\ldots\ldots \quad (15)$$

without making any presumption as to the nature of the slag sulphur. The apparent neutral effect of ferrous oxide in the Basic Open Hearth range has been first explained by Richardson[66] and subsequently by several other workers.[66,66,65] It causes an increase in oxygen activity in the iron and, being a basic oxide, an increase in the

ratio $(a_{O^{--}})/(\nu_{S^{--}})$. The first effect hinders and the latter favours desulphurization. In the Basic Open Hearth range of iron oxide contents (3 - 25 mol %), both these change at the same rate so that $(\%S)/[\%S]$ is substantially constant. And at low concentrations of iron oxide, as are encountered in the Blast Furnace (up to 0·1 mol %) and Electric Arc Furnace (0·1 to 3 mol %), $(\%S)/[\%S]$ falls with additions of iron oxide due to the faster increase in $[a_O]$ than $(a_{O^{--}})/(\nu_{S^{--}})$. This has also been illustrated by Shanahan[50] by means of a plot of $(\%S)/[\%S]$ vs (FeO) for constant slag basicity. A rectangular hyperbola was obtained showing $\frac{(\%S)}{[\%S]} \times (FeO)$ to be constant.

The effect of (FeO) on $(\%S)/[a_S]$ for various basicities is shown in Fig. 1. The data includes that of Bardenheuer and Geller[21], Hatch and Chipman[28], and Rocca, Grant and Chipman[37] which indicates the inverse dependence of sulphur distribution ratio on the FeO content at low percentages with a 45° slope and independence in the Open Hearth range.[48] A transition between these two types of behaviour occurs under Electric Arc Furnace conditions, which are ideal for the manufacture of low-sulphur steel.

Rocca, Grant and Chipman[37] investigated sulphur distribution between metal and slags of the Electric Arc Furnace type. A minimum value was obtained in the plot of distribution ratio v. iron oxide

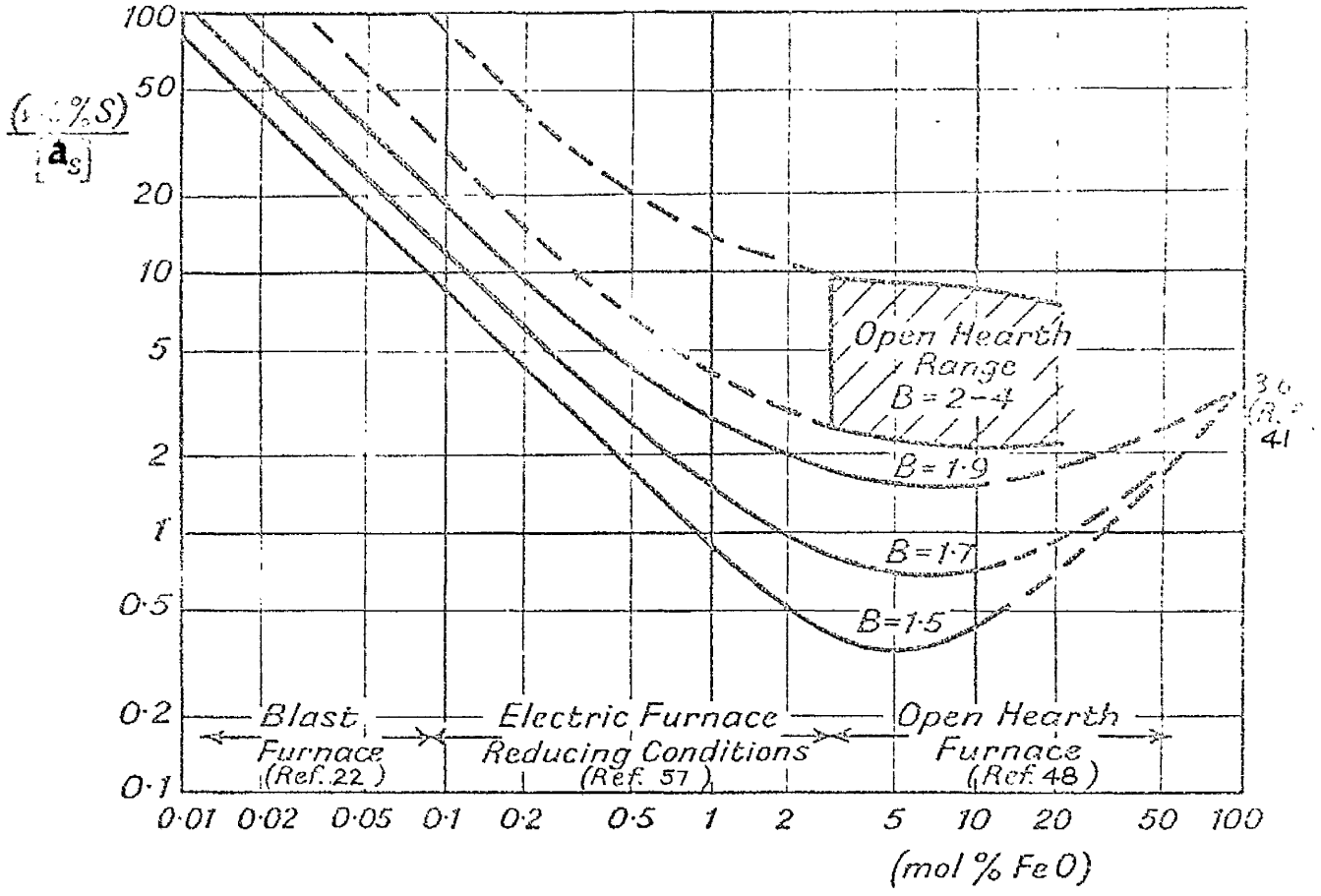


FIG. 1 Diagram showing the influence of basicity and of iron oxide content of the slag on the distribution of sulphur between slag and metal at 1600°C. The lower curves refer to acid slags with values of the molar acid : base ratio, $B = (CaO + MgO)/(SiO_2 + Al_2O_3)$, of approximately 1·5, 1·7 and 1·9. The range of basic open-hearth slags with B between 2 and 4 is shown cross-hatched (after Rocca, Grant and Chipman[57]).

constant and it became much flatter with increase of basicity. They used the Wentrup-type[28] of calculation, viz.

$$\frac{(\%S)}{[a_S]} = L_{FeS} + K' \frac{(\text{excess CaO})}{(\text{mol \% FeO})}$$

where $L_{FeS} = \frac{(\%S_{Fe})}{[a_S]}$ and $K' = \frac{(\%S_{Ca})}{[a_S]} \cdot \frac{(\text{mol \% FeO})}{(\text{excess CaO})}$

to trace the curves of basicities 1·5 and 1·7. The curve with basicity 1·9 is purely hypothetical.

The sulphur distribution reaction, although realised to be rapid normally, is very slow indeed in presence of carbon. This is due to the slow reduction of silica by carbon. Equilibrium sulphur partition is only attained when equilibrium is also reached between silica in the slag and silicon in the metal. As long as silica reduction takes place the pO_2 of the metal/slag system will not reach equilibrium with carbon and CO at one atmosphere. This will be reflected in slag FeO contents higher than those in equilibrium with carbon until SiO_2/Si equilibrium is reached. The most significant work in sulphur equilibrium under blast furnace conditions was carried out by Hatch and Chipman[29], and later by Taylor and Stobo[30].

Hatch and Chipman[29] studied the equilibrium using an induction furnace. Since the crucible was made of graphite, little or no induction stirring could be expected and so a stirring device was employed to aid the approach to equilibrium. This did not have

much effect, for the equilibrium time was often 7 h. Equilibrium was approached from slag or metal side by adding CaS to the slag or FeS to the metal respectively. The temperature was measured by an optical pyrometer standardised against a Pt -Pt(10% Rh) thermocouple and carbon monoxide was used as the furnace atmosphere to establish a P_{CO} of one atmosphere. The overall reaction could be written as:-

$$S + O^{--} + C = S^{--} + CO_{(g)} \quad \ldots\ldots\ldots \quad (20)$$

Rafeh and Chipman investigated the effect of total sulphur, slag basicity and temperature on desulphurization. In order to improve the correlation between the distribution ratio and "excess base", they redefined the parameter

"Excess Base" $= (n_{CaO} + \frac{2}{3} n_{P_2O_5}) - (n_{SiO_2} + n_{Al_2O_3})$

where n = number of mole of oxide per 200 g slag. This indicated that 1 mol of magnesia was equivalent to only $\frac{2}{3}$ mol of lime in considering desulphurization. The effect of temperature was small, although increase in temperature appeared to favour desulphurization. It was observed that the sulphur concentration in the metal is not directly proportional to the slag sulphur, alumina acts like silica in reducing the desulphurizing power of a basic slag while in the more acid slags it is less harmful than silica.

This work was open to criticism[67]. Thermodynamic calculations showed that the excess base expression overestimated slag basicity and the distribution ratios were susceptible to large

errors due to metal sulphur being low in presence of carbon with consequent inaccuracy in its determination. Considerable difficulty was experienced in removing the "shot" iron particles in the slag and estimating the iron oxide content of the slag. In spite of these remarks, it is the best available data on slag-metal sulphur distribution between blast furnace type slags and carbon-saturated iron, and reasonable correlation has been achieved with gas slag work as discussed earlier.

In the discussion of this paper, Rosenqvist[50] has explained the reason for the higher theoretical distribution ratio calculated by Hatch and Chipman compared with their experimental value (viz., 50 times as great) in the light of standard states for FeS and CaS. The theoretical distribution ratio is based on free energy calculations where dilute solutions of FeS and CaS are taken as the standard states. However, assuming pure solid CaO, solid CaS, and pure liquid FeS as standard states, Rosenqvist was able to show that this discrepancy is only four-fold. A better agreement can be obtained assuming positive deviation from Raoult's law for the activity curve of calcium sulphide as suggested by Rosenqvist. This is in line with the incomplete miscibility of liquid silicate and sulphide phases.

At this time no data existed on the effect of carbon and silicon on the activity coefficient of sulphur in iron and so inter-

pretation of the results was rather restricted. This was made available by the later work of Sherman and Chipman[18], and Morris and Buehl[7]. Taylor and Stobo[80] now reinvestigated this equilibrium because there was uncertainty as regards attainment of equilibrium in presence of carbon and the oxygen potential controlling the equilibrium. The latter doubt arose due to the difference in FeO analyses as reported by various sources. Their results indicated that there was no temperature effect in the range 1425 - 1550°C on sulphur distribution and the slight increase observed by Hatch and Chipman has been explained on the basis of increase of carbon and silicon in the metal with temperature. Rosenqvist[80], however, has indicated a 60% increase in the reaction constant with the rise of temperature from 1450 - 1550°C. If both sets of datnare reliable, this discrepancy could be explained only on the basis of large changes in the activity coefficients of lime and calcium sulphide. A calcium sulphide solubility of 1% in slags was obtained by these workers, which was lower than that obtained by Filer and Davies[106] on Blast Furnace slags (Ca 3·5 - 4·5% sulphur). It has thus been established that the equilibrium reached was with the C - CO potential. The agreement between their results and those of Hatch and Chipman[80] was good.

Of recent years, interpretation of slag-metal sulphur

distribution in terms of ionic concept has become more popular because of its simplicity and general applicability. These have been reviewed in detail elsewhere[48,58]. The X-ray work on glasses, conductivity, transport and E.M.F. measurements on molten slags have stimulated thought in this direction. The liquid slag being considered as a disordered version of the solid slag, but the concept of the ionic sites differed. Thus, Baraczynski[59] assuming a random distribution of cations and anions irrespective of their sign or charge, defined the ionic fraction as,

$$N_{M^+} = \frac{n_{M^+}}{n_{M^+} + n_{X^-}}$$

where, M^+ and X^- are the cations and anions respectively. Temkin[60] accounted for the electrostatic binding forces in his model by defining the ionic fraction as,

$$N_{M^+} = \frac{n_{M^+}}{n_{M^+} + n_{M^{2+}} + n_{M^{3+}} + \cdots}$$

Realising that a divalent cation is equal to an adjacent pair of monovalent cations and that the energies of interaction of the various ion-pairs are different, Flood, Forland and Grjotheim[61] redefined the ionic fraction as

$$N_{M^{2+}} = \frac{2n_{M^{2+}}}{n_{M^+} + 2n_{M^{2+}} + 3n_{M^{3+}} \cdots}$$

Whether the liquid slag can be regarded as completely ionic is a disputed question, however, the concepts have been applied to

sulphur equilibrium with encouraging results. Herasymenko and Speight[80] found that their equilibrium quotient K'_S for the reaction

$$\underline{O} + S^{=} = O^{=} + \underline{S} \quad \ldots\ldots\ldots \quad (15b)$$

does not depend on slag composition and can be represented by the equation

$$\log K'_S = \log \frac{[S](O^{=})}{[O](S^{=})} = \frac{6500}{T} - 2{\cdot}625$$

Thus the equilibrium can be expressed using simple ionic fractions and without activity coefficients. A similar conclusion for sulphur equilibrium was arrived at by Temkin[81] who assumed that the slag was a simple ionic solution and defined the activity of any constituent in slag as the product of its ion fractions.

In order to calculate sulphur distribution in Basic Open Hearth heats, Herasymenko and Speight[80] constructed nomograms relating the distribution ratio with the total acids defined by

$$\Sigma a = SiO_2 + 0{\cdot}634\ P_2O_5 + 0{\cdot}9\ Al_2O_3 \ (\%)$$

for various ion oxide contents.

Flood et al[80] showed that an anionic equilibrium depends on the cationic slag composition and vice versa by means of a cyclic treatment. For the sulphur equilibrium the mixed equilibrium quotient can be written as,

$\log K'_{1s} = N'_{Ca} \log K'_{Ca} + N'_{Fe} \log K'_{Fe} + \ldots\ldots$

for the reaction $\underline{S} + O^{--} = S^{--} + \underline{O}$ ..... (15)

where K'_{Ca}etc are the "equilibrium constants" when only lime is taking part in desulphurization and so on. K'_{1s} was found to be independent of slag composition for the sulphur equilibrium. This treatment assumed ideal behaviour in liquid slags, i.e. any correction term for activity coefficient, $f(\nu)$, = 0 and it does not account for the atomic interactions in liquid steel. The first assumption is clear from the higher than "ideal" activity coefficients of manganese oxide in silicate melts[80]. However, the additional assumption that silicon, a luminium and ferric iron are present only as SiO_3^{--}, AlO_3^{-3} and FeO_4^{-5} ions respectively, is not so serious in a basic slag.

Extending Flood's treatment further, Ward[80] has shown that $\log K^* = \sum_{1}^{i} N_i \log K_i^* + f(\nu)$

where,

K^* is a modified equilibrium quotient obtained by accounting for the interaction of solute elements in liquid metal and based on Henrian standard state i.e. $K^* = \dfrac{(N_S^{--})[a_O]}{(N_O^{--})[a_S]}$

1 = ... i are the cations present

and $f(\nu)$ is the activity coefficient term.

A comparison of the equilibrium quotient for the reaction (15)

as compiled by Carter[66], Ward[65] and from the recent research work of Sasonov and Shalimov[64] can be made the following table:-

Calculation made by	K'_{1s}	experimental data used for calculation
Tenkin et al	0·017	Fetters and Chipman
Narasymenko and Speight	0·014	Grant and Chipman
Flood et al	0·022	Grant and Chipman
Carter	0·021	Grant and Chipman
Sasonov and Shalimov	0·0221	Sasonov and Shalimov

TABLE I - COMPARISON OF EQUILIBRIUM QUOTIENTS

$$K'_{1s} = \frac{(N_S^{-2})}{(N_O^{-2})} \frac{[wt\%O]}{[wt\%S]}$$

Turkdogan[64] has compared the desulphurising power of slags through the function called 'sulphur capacity' of the slag and is defined as

$$\Lambda_S = \frac{(N_S)[a_O]}{[a_O]}$$

where, (N_S) = ionic fraction of sulphur in the slag. This is a function of the sulphide capacity, C_S, of the slag and is related to the sulphur capacity index given by

$$\lambda = \frac{1}{N_{SiO_2} + 1.5\,N_{P_2O_5} + 1.3\,N_{Al_2O_3}}$$ for given temperature.

Both $\log \Lambda_s$ and $\log C_S$ were found to be linear functions of $\frac{1}{T}$ for given value of λ.

By analogy to 'sulphide capacity', C_S, Chipman et al[60,66] have arrived at a function called 'S - O ratio' i.e. $\frac{(\%S)}{[\%S]} = [\%O]$, which, like the former, is proportional to $(a_{O^{--}})/(\gamma_{S^{--}})$. Bishop, Lander, Grant and Chipman[60] plotted this ratio against mol % SiO_2 and found that it decreases almost linearly with increase in silica. This is in line with the trend of 'S - O' ratio with mol % SiO_2 calculated from gas-slag work of St. Pierre and Chipman[66], and Pinchan and Richardson[10]. The good correlation between 'S - O ratio' and mol % silica suggests that the ratio $(a_{O^{--}})/(\gamma_{S^{--}})$ is nearly independent of the ratio $\frac{(\text{mol \% lime})}{(\text{mol \% } FeO_T)}$. Their results also showed that the plot of $\frac{(\%S)}{[\%S]}$ versus basicity expressed as $\frac{CaO + MgO + MnO}{SiO_2 + Al_2O_3 + P_2O_5}$ decreases with increase in (FeO_T) for basicities greater than 2·4. On replotting the data in a pseudoternary diagram, it was found that the iso-sulphur distribution lines are roughly parallel to the line joining the ferrous oxide to the orthosilicate composition, especially in the higher basicity side. These observations are in accordance with the work of Grant and Chipman[48].

In a later investigation, Bishop, Grant and Chipman[63] established the effect of temperature and magnesia in slags of the system $(CaO-SiO_2-FeO_t)$ on the distribution coefficient by studying the reaction in lime and dicalcium silicate crucibles.

using an induction furnace. They found that magnesia up to 10 mol % did not appear to have any effect on the distribution ratio, it decreased slightly from 11 to 10 as the temperature increased from 1530 to 1700°C in lime saturated iron oxide slags. This temperature dependency on the distribution ratio is in good agreement with the value of 10·3 calculated from the results of Bardenheuer and Geller[41] using the expression.

$$\frac{(\%S)}{[\%S]} = 3{\cdot}1 + 13{\cdot}3 \left\{\frac{\text{wt. \% CaO}}{\text{wt. \% FeO}}\right\}.$$

The standard free energy change for the reaction

$$\underline{S} + (O^{=}) = (S^{=}) + \underline{O} \qquad \ldots\ldots\ldots\ldots \qquad (15)$$

is given by,

$$\Delta G^{\circ}_{15} = 17{,}200 - 9{\cdot}12T$$

and $\log K'_{15} = \log \frac{(\%S)}{[\%S]}[\%O] = -\frac{3750}{T} + 1{\cdot}956.$

for lime-saturated iron oxide slags. This value is in good agreement with the free energy for the same reaction

viz., $\Delta G^{\circ}_{15} = 18{,}000 - 9{\cdot}25T$

calculable from the results of Bardenheuer and Geller[41].

Mechanism of Sulphur Transfer

The mechanism of sulphur transfer from metal to slag has been much discussed[37,55,56,60]. The exchange of sulphur from metal to slag takes place by a reduction mechanism and is supported from

kinetic studies[66,80]. Indeed, it is very slow in presence of carbon. Darge, Philbrook and Goldman[66], in their reaction rate studies, plotted the concentration of sulphur and iron in the slag with time and observed a peak in the iron curve. The sulphur curve increased initially and reached a constant value. This is indicative of the following mechanism.

$$[FeS] = (FeS) \quad \text{.....} \quad (16)$$

$$(FeS) + (CaO) = (CaS) + (FeO) \quad \text{.....} \quad (17b)$$

$$(FeO) + \underline{C} = Fe(\ell) + CO_{(g)} \quad \text{.....} \quad (21)$$

Alternatively, Rosenqvist, in the discussion of the paper by Darge et al, suggested the exchange of sulphur and oxygen via the slag&metal interface, followed by the carbon-oxygen reaction.

$$\underline{S} + O^{--} = \underline{O} + S^{--} \quad \text{.....} \quad (15)$$

$$\underline{C} + \underline{O} = CO_{(g)} \quad \text{.....} \quad (22)$$

Chipman et al considered reaction (16) as controlling desulphurization under steel making conditions[80] and reaction (17b) or (17) as operative under reducing conditions[82]. Carter[66] preferred the ionic mechanism (15) for slags of high or low FeO content. Recently, Ramachandran, King and Grant[66] studied the anodic and cathodic reactions taking place along with sulphur transfer. All these observations are summarised in the adjoining diagram.

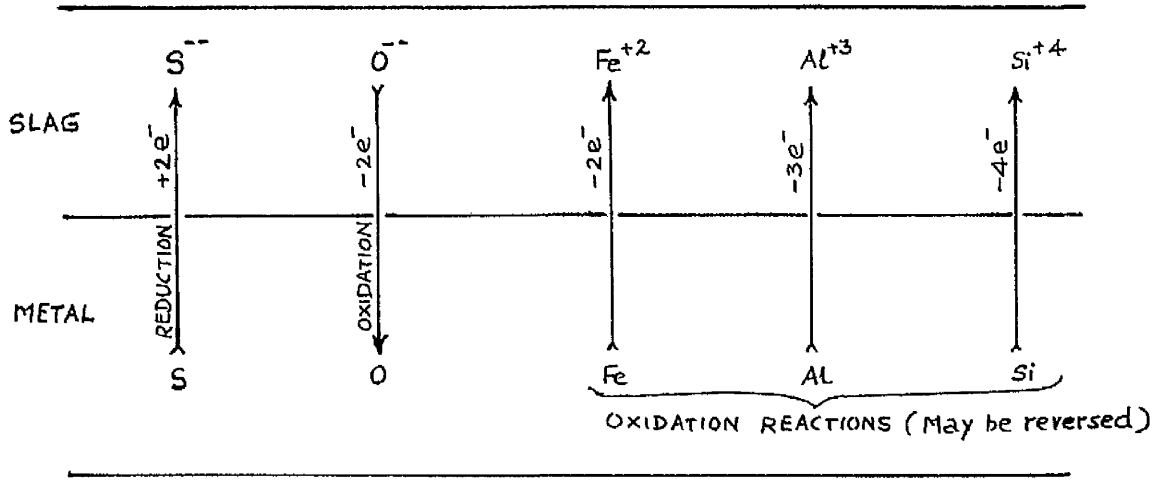


Fig. 2 - DIAGRAM ILLUSTRATING SLAG-METAL SULPHUR TRANSFER

Since the reduction mechanism is balanced by one or more of these oxidation reactions, the factors leading to high equilibrium sulphur partitioning are those which favour one or more of these oxidation reactions. Generalising, they are high activity coefficient of sulphur in the metal, low activity coefficient of sulphide ions in the slag, high oxide ion activity in the slag and/or low metal oxygen activity.

CHAPTER XII

EXPERIMENTAL METHOD

EXPERIMENTAL METHOD

1. CRUCIBLES

One of the biggest practical problems which faces one interested in equilibrium studies at elevated temperatures, be it gas-slag, slag-metal or gas-metal work, is to find a suitable container. While noble metal containers, such as platinum or iridium, have been developed satisfactorily in recent years to study gas-slag equilibrium distribution of sulphur, these cannot be used for slag-metal work for fear of formation of alloys. It is almost impossible to measure slag-metal sulphur partition experimentally without introducing some complication into the system.

The use of graphite crucibles for the study of slag-metal sulphur partition offered two distinct advantages. Firstly, the oxygen potential of the system being studied can be fixed, equating p_{CO} to unity and thereby simplifying the reaction. This can also be a restriction since it does not allow the system to be studied at different oxygen potentials. Secondly, there occurs little or no crucible reaction with the constituents of the slag, thereby eliminating the introduction of a third or fourth component into the slag. Such crucibles were used by Hatch and Chipman[28] as indicated earlier. The first disadvantage, however, is the long equilibration time needed. This is due to the slow reduction of silica by carbon. The question of absolute attainment of equilibrium in carbon crucibles should, therefore, be regarded with

some reservation only. This has been confirmed recentlyby Gibbons[88]. Further, the discrepancy in correlation of the results of Hatch and Chipman[84] with those calculated from gas/slag data can be explained by the non attainment of equilibrium with respect to the partition of silicon between slag and metal. The second feature of the experiments of Hatch and Chipman is the inclusion of tiny droplets of iron in the slag which made the assessment of the iron-oxide content of the slag difficult. After a simple magnetic separation, they gave a value of 0·2% FeO in the slag. The slags were again subjected to a vigorous magnetic treatment with the aid of a Franbs Isodynamic seperator and values of the order of 0·03 % FeO were obtained. This appeared quite reasonable, since a_{FeO} in equilibrium with a carbon saturated iron-carbon binary alloy at 1500°C and 1 atmospheric pressure of carbon monoxide is 0·02%[20]. A third point against the use of carbon crucibles is the low percentage of sulphur in the metal obtainable in presence of carbon due to the increased activity coefficient of sulphur in presence of carbon and silicon in the metal. This causes analytical difficulties by the usual oxygen combustion method for sulphur and brings in large discrepancies in the distribution ratios when two analyses of the same metal sample were carried out This is evident from the following table by Hatch and Chipman:-

	(% S)	First Analysis [%S]	First Analysis (S)/[S]	Second Analysis [%S]	Second Analysis (S)/[S]
H M 19 d	1·59	0·006	265	0·005	318
H M 44 6	2·25	0·006	375	0·007	322

TABLE 2 - SULFUR ANALYSES OF SLAG AND METAL SAMPLES OF HATCH AND CHIPMAN

In view of these problems, a different crucible was sought and a satisfactory solution was found in calcium sulphide and magnesia crucibles.

(a) Calcium sulphide crucibles :-

It was proposed to use calcium sulphide crucibles to study slag-metal sulphur distribution. This appeared very attractive because an exact picture of the thermodynamics of sulphur partition can be obtained in terms of the ratio of the activity of sulphur in the slag and the metal rather than $(\%S)/[\%S]$. While $[a_S]$ is calculable from $[\%S]$ using the data of Sherman, Elvander and Chipman[a], a_{CaS} could be equated to unity since the slag would then be saturated with calcium sulphide. The equilibrium constant for the reaction,

$$(CaO) + \underline{S} = (CaS) + \underline{O} \qquad \ldots\ldots\ldots\ldots \qquad (23)$$

is then simply

$$K_{23} = \frac{[a_O]}{[a_S](a_{CaO})}$$

Thus a_{CaO} values could be computed at CaS saturation level. Moreover, the puzzling feature of the uncertainty of assessment of the activity coefficient of calcium sulphide could be avoided.

The high temperature properties of refractory sulphides are well known and their utility as high temperature refractory materials has been discussed by Blocher[67]. They offer a fertile field for high temperature work despite their susceptibility to oxidation at red heat. They could be used in an inert or reducing atmosphere with advantage. The reasonably high melting point of most sulphides, suitable thermodynamic properties, reasonably high density, resistivity and magnetic susceptibility make them a suitable choice for high temperature work. Of these, the free energy of formation is of great significance as it decides not only the decomposition of the refractory body, but also the possibility of contaminating the metal contained in the crucible. Obviously, a low free energy of formation is desired. Density is of importance as it relates to the porosity of the refractory body after firing, while the resistivity and magnetic susceptibility are of value as aids in determining the induction characteristics and in indicating the type of bonding. The volatilities of some of the sulphides, however, limit their

application for high vacuum work.

Blocher[67] reports the use of sulphides as versatile containers for melting high purity metals. Thus, metals like uranium and cerium have been melted in barium sulphide crucibles with little or no pick up of sulphur from the crucible. So also experimental fusion in cerium and thorium sulphide crucibles have been successfully attempted for a wide range of metals without contamination. However, these have not been put to study slag-metal sulphur partition for their resistance to molten slags was unknown.

The attack of the slag on the crucible can be deduced from the solubility of calcium sulphide in slags. No accurate data for the solubility of sulphide in slags are yet available but the approximate data presented by Carter and Macfarlane[40], combined with those of Gibbons[82], and Sharma and Richardson[84], are reproduced in the following table.-

Investigators	Approximate Slag Composition				Temp. °C	(%S)
	CaO	Al_2O_3	SiO_2	MgO		
McCaffery and Ontario	Range of Compositions				1500	8 - 11
Glaser	48	-	52	-	1500	5·5
Filer and Derkon	41	15	37	7	1500	3·5 - 4·5
Taylor and Stobo	29	45	26	-	1500	1
	39	19	37	5	1475	4
Fincham and Richardson	41	52	7	-	1500	~2
Martin, Glockler and Wood	46	13	41	-	1425	3·6
Carter and Macfarlane	52	48	-	-	1500	~2·7
Gibbons	50·5	49·5	-	-	1550	1·8
	45	55	-	-	1550	4
	54	32·5	14	-	1550	4·5
Sharma and Richardson	42	58	-	-	1500	0·58
	56	44	-	-	1500	1·62

TABLE 3 SOLUBILITY OF SULPHUR IN SLAGS

Thus from the point of view of solubility, calcium sulphide seemed quite a reasonable crucible material.

Of the various methods of fabrication of ceramic bodies, viz., powder pressing, ramming, extruding and slip casting, the powder pressing

method has been tried in the past with success for sulphide crucibles. High strengths and high densities can be obtained by powder pressing techniques. However, the addition of various materials to serve as temporary binders or lubricants was necessary. For example, barium sulphide crucibles have been prepared by ball milling the lumps to 200 to 300 mesh particle size, mixing with 5 volume percent of naphthalene as binder and plasticizer , after which it is pressed in tapered steel molds and dies using 80,000 to 100,000 p.s.i. After removal of the binder by heating to 150°C in vacuum, the green crucible was fired in a vacuum furnace capable of maintaining a pressure of $< 10^{-3}$ mm and preferably 10^{-6} mm of mercury. Firing barium sulphide crucible was done at temperatures between 1450 and 1650°C. Firing below 1450°C resulted in a powdery crucible which is more reactive toward moist air than those fired at higher temperatures. The same procedure can be applied with success to calcium sulphide crucibles. It has been reported in the case of barium sulphide crucibles that the use of naphthalene as bond could, however, be dispensed with if higher pressures were used. Slip casting of sulphide crucibles has not been tried so far.

Slip-casting is an elegant technique for the manufacture of refractory crucibles, for it is quick and inexpensive. Thomson and Mallot[66] have demonstrated that this process could be applied for the production of oxide refractory crucibles in two ways. Those

materials which lacked the property of plasticity were finely ground and treated with acid before being slip cast. By this means, plasticity was developed in beryllia, alumina, thoria, zirconia and zircon. Secondly, for those materials which hydrated with water, a non-aqueous medium was used to overcome the damaging effects due to hydration. Magnesia crucibles,for example, are slip cast satisfactorily today using absolute ethanol or methanol. Slip casting calcium sulphide crucibles to study slag-metal sulphur partition formed the preliminary part of the present investigation.

While slip casting is a technique in itself, preparation of calcium sulphide crucibles required much more skill. Although absolute ethanol (or methanol) was the obvious choice, little plasticity was developed even when the slurry was in contact with the medium overnight. Hence various binding agents were sought. These were of two general types.

(a) Organic substances which were completely burnt out or evaporated during firing, e.g. naphthalene, dextrin and tragacanth.

(b) Calcium compound of organic acids which is converted during firing to the metal oxide, e.g. calcium stearate. The use of plaster of paris mould did not prove satisfactory in the beginning for, crucibles prepared in this way stuck to the mould walls and could not be taken out even when using French chalk in the beginning to dust the mould walls. Attention was therefore focussed on filter

paper extraction thimbles. Greenway[66] has used this method extensively for slip casting magnesia crucibles, the thimble being burnt off during firing. When success was achieved with extraction thimbles, Plaster of Paris moulds were again tried. It was found that the consistency of the slurry and the time it is in contact with the mould were as critical as the water content in the 'absolute' ethanol. Crucibles were slip cast in this way with greater difficulty than with extraction thimbles. Moreover, the use of binder was also dispensed with in later stages. The following procedure was adopted in order to prepare satisfactory crucibles with a flat or round bottom.-

Absolute alcohol (ethanol) with a water content of < 1% has been found to be quite suitable for the production of calcium crucibles. Technical grade calcium sulphide (supplied by M/s Hopkin and Williams) was used without any further grinding, because it was very fine. It was intimately mixed with absolute alcohol using a mortar and pestle with or without 5 volume percent of binder, adding alcohol a little at a time until a thin slip was produced. Care was taken to avoid formation of lumps. This was transferred to a bottle and the procedure was repeated. When sufficient slurry has been prepared to produce 15 or 20 crucibles, about 20 volume per cent more of alcohol was added to the bottle. The contents were shaken several times and kept overnight out of contact with air.

The next morning, the excess alcohol was drained into a beaker. The slurry which was very thick was transferred into the mortar, and was mixed very well adding the alcohol carefully until it has the same consistency as a sugar syrup. This was quickly poured into a good plaster mould dusted with french chalk or into a filter paper extraction thimble, filling the cavity to three quarters. When a sufficient thickness of crucible was formed by absorption of alcohol by the mould walls or extraction thimble, the superfluous slip was decanted into the mortar and used to make the next crucible.

Considerable difficulty was encountered in removing the crucible from the mould, because they had little or no shrinkage in the mould due to absorption of the alcohol. Compared to the shrinkage of magnesia, the shrinkage of calcium sulphide in the mould was far less, it was far more when the crucible was fired. Adjusting the consistency of the slip and the time it was in contact with the mould (which was obtained by experience) the crucible could be easily taken out. However, the first two crucibles broke down when they were taken out from the mould. Although the extraction thimble was burnt out during firing to prepare round bottomed crucibles, attempts were made later with success to take out the crucible and save the thimble. The plaster mould was allowed to dry for 15 minutes after the production of a crucible and in this way

about eight crucibles at a stretch could be prepared from the same mould, after which it was allowed to dry overnight before being used again. The green crucibles were extremely fragile and were dried for a day or two, being kept in a desiccator before being fired.

Firing calcium sulphide presented many problems. This was carried out very slowly in two stages, first at 1000°C for a few hours or preferably overnight in batches of six crucibles and finally at 1700°C for 2 to 4 h one by one. A horizontal nichrome wound furnace was found suitable for preliminary firing. A few of the preliminary fired crucibles were subjected to final firing in a horizontal platinum - 20% rhodium resistance furnace, but the majority of them were fired in a special molybdenum muffle furnace built in the department. The latter was designed such that the crucible as well as the molybdenum winding were protected from oxidation by the zone atmosphere of cracked ammonia. The temperature of the crucible during firing was sighted using an optical pyrometer. The firing, however, had to take place in three stages when naphthalene was used as the binder, the first firing being done at 150°C for an hour so as to volatilize all the binder.

Pure argon was used as the protective atmosphere for few crucibles in the beginning for preliminary firing, but was soon replaced by hydrogen atmosphere for two reasons. With use of argon, copious evolution of sulphur dioxide took place at about 900°C which bubbled

through the delivery tube. Moreover, the crucibles when stored for 10 days developed cracks and crumbled to powder. A green mass was found sandwiched in the walls. With hydrogen very little or no sulphur dioxide was formed on slow firing and the crucibles were more stable. Thus hydrogen was the inevitable choice for preliminary firing. However, in both these atmospheres, hydrogen sulphide was evolved at about 900°C. Other observations which were made during preliminary firing were, sulphur deposits in the furnace and delivery tube formed at about 650°C, the collection of droplets of water in the exit tube, and black deposits of carbon on the outside of the crucible when naphthalene was used as the bond.

No difficulty was experienced in the final firing in the platinum-rhodium furnace using a hydrogen atmosphere or in the molybdenum muffle furnace in an atmosphere of cracked ammonia. The crucibles especially after preliminary firing were stored in desiccators since they absorb moisture from the atmosphere and develop cracks. Two crucibles slip cast in this way are shown in Fig. 3. The crucibles were white or ash coloured, mechanically strong and impervious to gases.

One puzzling feature about calcium sulphide crucibles is their contraction on firing. The size of the final crucible was only a third of the volume of the original crucible. Hence the mould design was a problem in order to manufacture crucibles which can go into the

Fig. 3 - Slip cast calcium sulphide crucibles using filter paper extraction thimble (left) and Plaster of Paris mold (right).

1.1/2" mullite reaction tube and at the same time accommodate as much metal and slag as possible.

Using the calcium sulphide crucibles prepared in this way, equilibration experiments were conducted at 1550°C with lime-silica or lime-alumina slags and molten iron. The crucible was charged with about 30 g of Armco iron in the form of two pellets, enclosed in a carbon crucible and the whole crucible assembly heated to 1550°C in a platinum furnace using an atmosphere of argon. Iron melted at 1535°C and the crucible held molten iron for an indefinite period. Thus the performance of the crucible to hold molten iron was very satisfactory. About 5 g of lime-silica or lime-alumina slag was added right into the crucible using a [illegible]steel tube. Molten iron could be maintained in contact with molten slag for about 20 minutes in argon atmosphere. After this period, either the crucible broke down or it was soaked with the slag exposing the metal, before any attempts to sampling were made. In this respect, the performance of the crucible with lime-alumina slag was found to be slightly better than with lime-silica slag.

The study of the effect of bonding on the performance of the crucible was next attempted. It was hoped that the performance could be better by a proper choice of bond and so various crucibles were prepared with different bonds - napthalene, dextrin, tragacanth and calcium stearate - for this purpose. These were tried one after

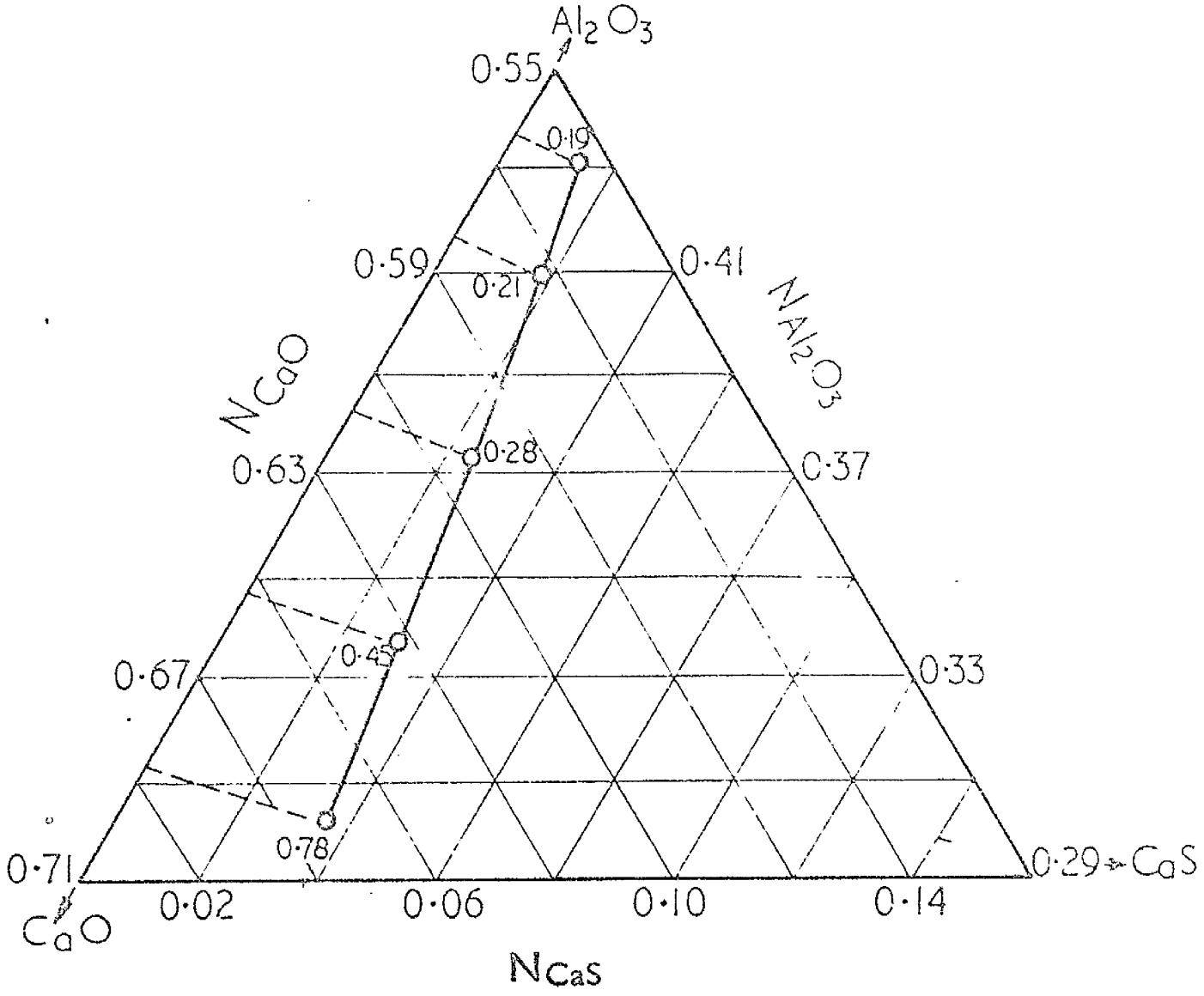


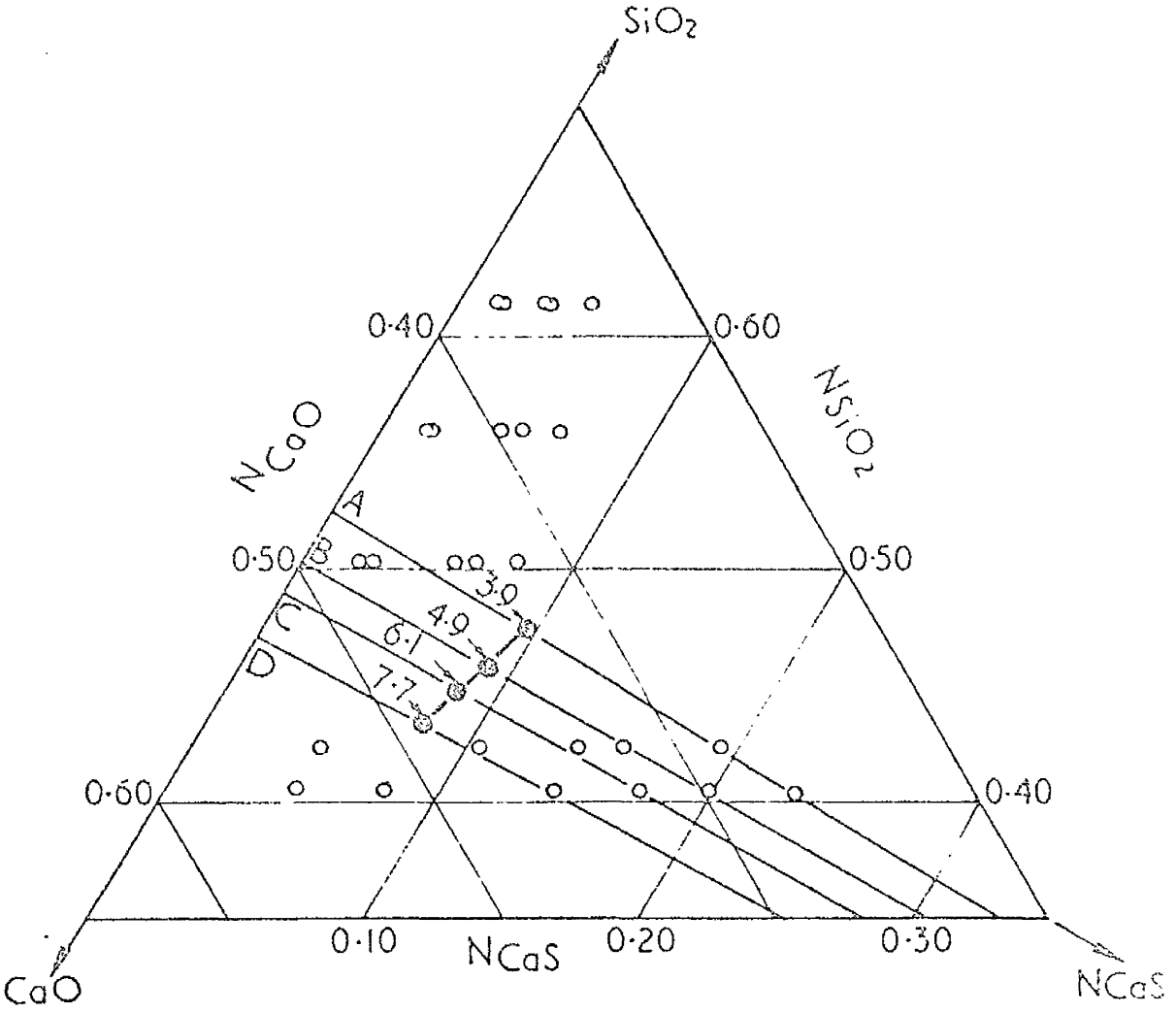
FIG 4 _ Saturation limits for CaS in the system $CaO-Al_2O_3-CaS$ at 1500°C. (After Sharma and Richardson[31])
Full line shows the solubility limits for CaS and the numbers opposite each point are the derived activities of lime relative to the solid.

another for equilibration experiments with iron and slag. It was found that these were no better than the crucibles without a bond.

It was felt, therefore, that saturating the slag with calcium sulphide before the run would decrease the dissolution of the crucible in the slag so that molten iron could be maintained in contact with the slag for greater length of time. The solubilities of calcium sulphide in the respective slags could be determined from the $CaO-CaS-Al_2O_3$[31] and $CaO-CaS-SiO_2$[34] ternary diagrams of Sharma and Richardson. These are reproduced in Figs. 4 and 5. For example, a lime-alumina slag of the composition 50 : 50, would dissolve as much as about 3% CaS (i.e. $N_{CaS} = 0.03$) at 1500°C. This is taken as a rough guide only as the working temperature is 1550°C. and the solubilities are expected to increase with temperature. In this way equilibration experiments were conducted with molten iron and slag saturated with calcium sulphide. But still the performance of the crucible was not satisfactory. On most occasions the slag soaked into the crucible and exposed the molten metal.

A possible explanation for the poor performance of the slip cast calcium sulphide crucibles and their abnormal behaviour on preliminary firing was therefore sought. Kept overnight in contact with absolute ethanol, part of the calcium sulphide could decompose to form ethyl mercaptan and lime as follows:-

$$CaS + C_2H_5OH = CaO + C_2H_5SH \quad \ldots\ldots\ldots\ldots\ldots\ldots (24)$$



each point represents one sample; figures show derived lime activities multiplied by 10^3

FIG 5. *Compositions obtained after equilibrium and the derived solubility limits (filled circles) for* CaS *in* $CaO + SiO_2$ *melts at 1550°C* (After Sharma and Richardson[34])

The formation of mercaptan in the slip was identified by its characteristic penetrating odour quite different from that of either ethanol or calcium sulphide. Although ethyl mercaptan was not available in the stores, more or less the same smell was perceived when sulphur was warmed gently with ethanol. Thus slip cast calcium sulphide crucibles contain some lime which is responsible for the development of cracks when they were stored after preliminary firing. This is due to the damaging effects of hydration on lime. It was suspected, however, that technical grade calcium sulphide might contain some excess sulphur as this might easily explain the formation of sulphur deposits in the furnace and the formation of hydrogen sulphide at about 500°C. Attempts were therefore made to assess the stoichiometry of calcium sulphides by subjecting to analysis by carbon dioxide combustion method of Fincham and Richardson.[71] The analysis so obtained was 34·98% sulphur compared with the theoretical value of 44·43% sulphur if calcium sulphide was strictly stoichiometric. Thus calcium sulphide (technical grade) is sulphur deficient and hence this is inadequate to explain these phenomena during firing. It appears from the analysis that technical calcium sulphide might contain some lime which could also contribute to the cracking of preliminarily fired crucibles. It is therefore tentatively suggested that the complications encountered during firing can be explicable only on the basis of reaction between the species. CaS, CaO, H_2 and the

adsorbed C_3H_5OH and C_2H_5SH.

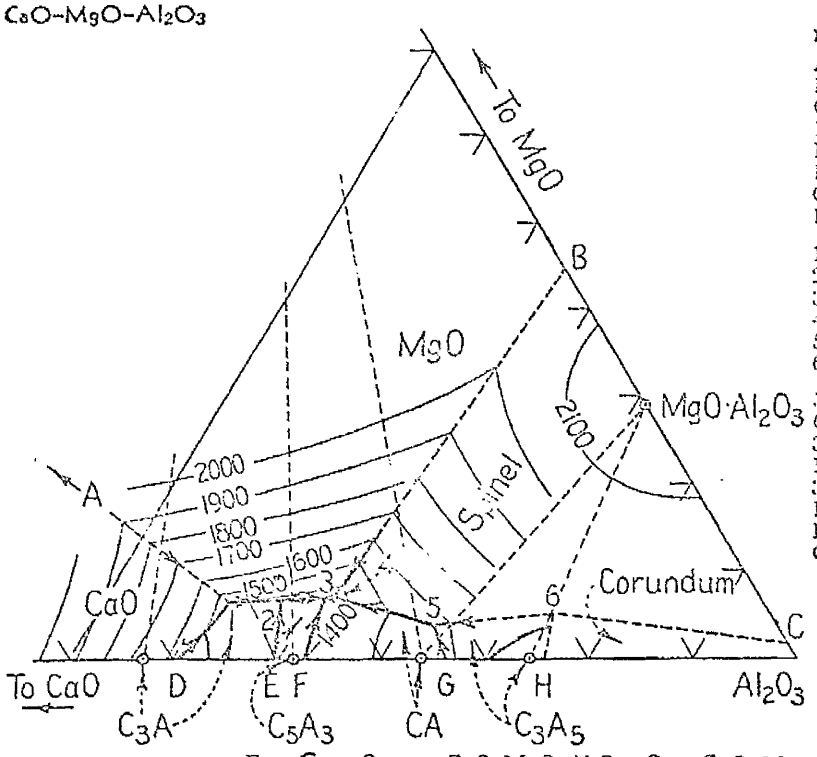
It has been seen that although every effort has been made to bring this project into practice, it met only with partial success. However, the hope that calcium sulphide crucibles could be used to study slag-metal reactions still exists. This might involve some modifications in the techniques adopted to manufacture calcium sulphide crucibles. For a very sturdy crucible, the particle adhesion is very important; this can be achieved by increasing the packing density of the powder and decreasing the particle size. It has been suggested that presintering the calcium sulphide powder at a very high temperature, say 1600°C, and ball-milling after breaking up the lumps followed by slip casting might produce better crucibles.

(b) Magnesia Crucibles

Magnesia crucibles of low permiability have been slip cast successfully in the same manner as calcium sulphide crucibles by the Thomson-Mallet method[60] using absolute ethanol. Fused magnesia ground in a rubber-lined ball mill using alumina balls for 36 or 48 hours and sieved through a 200 mesh screen formed the starting material. This material is ready for slip casting on mixing with absolute ethanol, as it develops plasticity immediately.

To obtain a good non-porous crucible, magnesia should be fired at 1700°C. After a preliminary firing at 1000°C in the department, they were fired further to this temperature in an oil

CaO–MgO–Al_2O_3



Pt.	Crystal Phases	CaO	MgO	Al_2O_3	Temp.
A	C, M	67.0	33.0		2[illegible]
B	M, MA		45.0	55.0	2[illegible]
C	MA, A		2.0	[illegible]	[illegible]
D	C, C_3A	59.0		41.0	1[illegible]
E	C_3A, C_5A_3	50.0		[illegible]	[illegible]
F	C_5A_3, CA	47.0		53.0	1[illegible]
G	CA, CA_2	33.5		66.5	[illegible]
H	CA_2, A	24.0		76.0	17[illegible]
1	M, C, C_3A	51.5	6.2	[illegible]	[illegible]
2*	M, C_3A, C_5A_3	46.0	6.3	47.7	1345
3*	M, C_5A_3, CA	41.5	6.7	51.8	1345
4	M, MA, CA	45.7	6.9	32.4	1370
5	MA, CA, CA_2	33.3	3.5	63.2	1550
6	CA_2, MA, A	21.0	5.0	74.0	1685
	$5CaO·3Al_2O_3$	47.8		52.2	1455
	$CaO·Al_2O_3$	35.4		64.6	1670
	$3CaO·5Al_2O_3$	24.8		75.2	1720
	$MgO·Al_2O_3$		28.4	71.6	2135
	$3CaO·Al_2O_3$	62.2		37.8	1535
	Periclase		100.0		2800
	Lime	100.0			2570
	Corundum			100.0	2050

* Eutectic.

FIG. 6 —System CaO–MgO–Al_2O_3; C = CaO, M = MgO, A = Al_2O_3.

G. A. Rankin and H. E. Merwin, *Z. anorg. u. allgem. Chem.*, 96, 309 (1916).

fired furnace by courtesy of J.G. Stein and Co., Ltd., Bonnybridge. Dense translucent crucibles obtained in this way were found very satisfactory for lime-alumina, lime-alumina-silica, and lime-iron oxide-silica slags, while they were less satisfactory for lime silica slags used in this investigation.

Moreover, a study of the ternary diagrams $CaO-MgO-Al_2O_3$ and $CaO-MgO-SiO_2$ (Figs 6 and 7) showed that for the slags investigated the solubility of magnesia was not too large, the maximum being about 12%. Thus magnesia appeared to be a good crucible material.

The advantages of using magnesia crucibles over graphite crucibles for slag-metal sulphur distribution work has been indicated earlier. In this case there is a definite attainment of equilibrium quickly and further the metal sulphur determination is more accurate, as it is higher. Moreover, the oxygen potential can be varied by using different amounts of ferrous oxide in the slag which can be determined with reasonable accuracy as the slag is nearly free from any admixture of iron particles. Thus as will be shown later, satisfactory correlation can be achieved with gas-slag work.

(2) MATERIALS

(a) Metallic Charge

Armco iron was used as the source of iron. The main impurities were:-

CaO–MgO–SiO_2

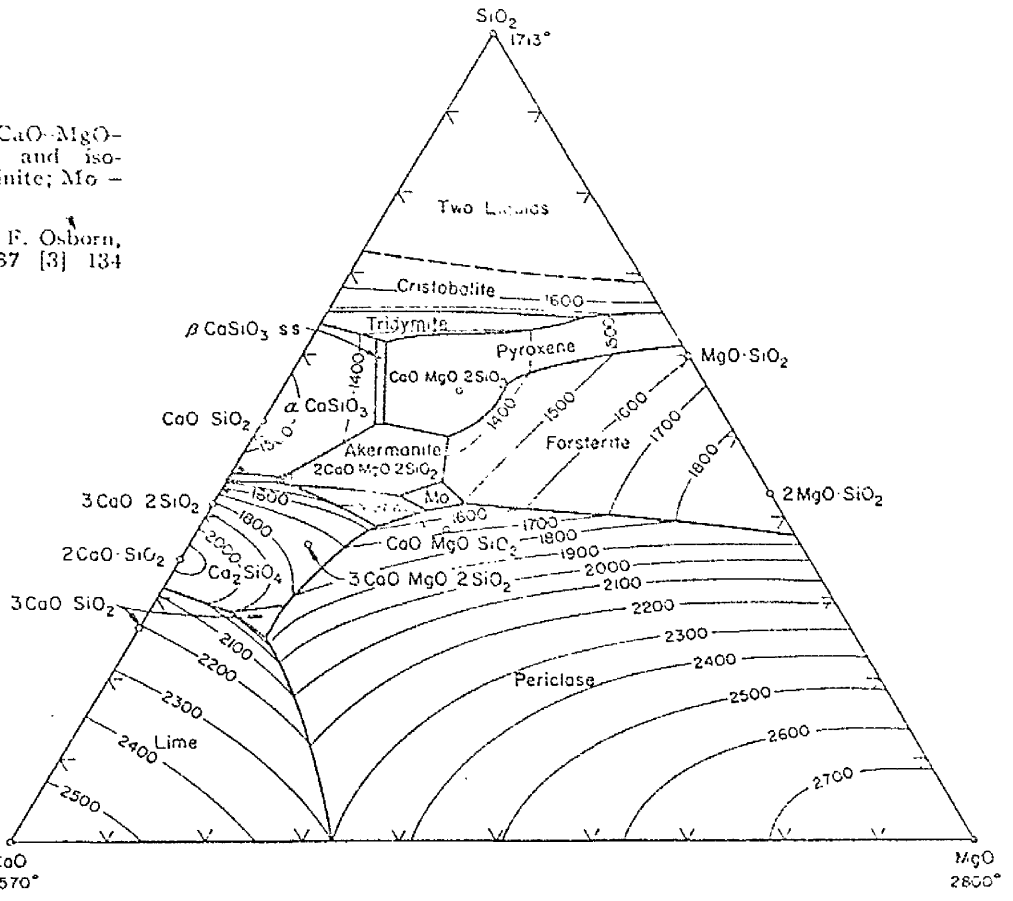


FIG. 7 System CaO–MgO–SiO_2 (primary phases and isotherms). Merw—merwinite; Mo—monticellite.

R. W. Rieker and E. F. Osborn, *J. Am. Ceram. Soc.*, 37 [3] 134 (1954).

C	Mn	P	S	Si
0·015%	0·017%	0·005%	0·025%	0·003%

Sulphur was added to the metallic charge as yellow sulphur.

(b) Slag

A majority of slags used in this investigation were lime/alumina slags of basic composition 55%, 50%, 45% CaO with varying amounts of iron oxide added. In some runs, lime/alumina/silica slags were used, by melting about 5% silica with the above slags. A few melts were tried with lime/silica slags of basic composition 56% and 53% lime. A number of preliminary runs were carried out by addition of varying amounts of iron oxide to these silicate slags.

These master slags were prepared from mixtures of "analar" substances. The appropriate quantities of substances were mixed well, pelletised, and melted for 10 - 15 minutes in a graphite crucible using an induction furnace. The molten slag was cast into a button mold. This was broken up and remelted to ensure complete homogenization. This was broken up again into small pieces and decarburized by heating for two hours in a muffle furnace at 1000°C. The slag so obtained was white or yellowish white in colour free from any carbon. The slag was finally crushed in a percussion mortar to pass a 30 B.S.S. sieve.

Sulphur was added to the slag as calcium sulphide and iron oxide was added as Fe_2O_3 to give the desired analysis.

(3) FURNACE ARRANGEMENT

In order to study the equilibrium distribution of sulphur between liquid iron and a range of synthetic slags a small platinum furnace was built in the department. The essential features of its construction are shown in Fig. 8.

The furnace consisted of a thin alumina tube B with 20 S.W.G. platinum wire D wound evenly over a length of 14". The platinum wire was covered with a 1/4" layer of alumina cement and was surrounded by fused alumina powder E enclosed in an outer alumina tube H. The space between this tube and the outer frame G was packed with diatomaceous insulating bricks. F. The reaction tube C was of mullite, 36" in length and 1.1/2" in internal diameter, supported at the top by two vertical steel supports fitted to the furnace case and at the bottom by means of a clamp (not shown in the figure). This tube was impervious to gases up to as high a temperature as 1700°C.

The magnesia crucible A was 1.6" high and about 0.8" in internal diameter with a wall thickness of about 0.1". This was enclosed in a graphite crucible B, 1.2" i.d. and 2.5" high with a wall thickness of about 0.1". This arrangement prevents fluxing of the mullite tube with the slag in case of breakdown of the magnesia crucible. The crucible assembly was placed in the hot zone of the furnace supported by alumina stools G resting on a rubber bung K at the bottom.

KEY

A	Magnesia Crucible (0.8" i.d 1.8" high)
B	Graphite Crucible (1.2" i.d 2.5" high)
C	Mullite Reaction Tube (1.5" i.d 36" long)
D	Platinum Winding (20 S.W.G)
E	Fused Alumina
F	Diatomaceous Bricks
G	Furnace Frame
H	Alumina Tube
I	Asbestos Insulation
J	Asbestos Radiation Shields
K	Rubber Bungs
L	Observation Window
M	Inlet For Argon
N	Outlet For Argon
O	Platinum - Platinum Rhodium Thermocouple
Q	Alumina stools
P	Mullite Sheath For Thermocouple
R	Power Terminals
S	Alumina Tube

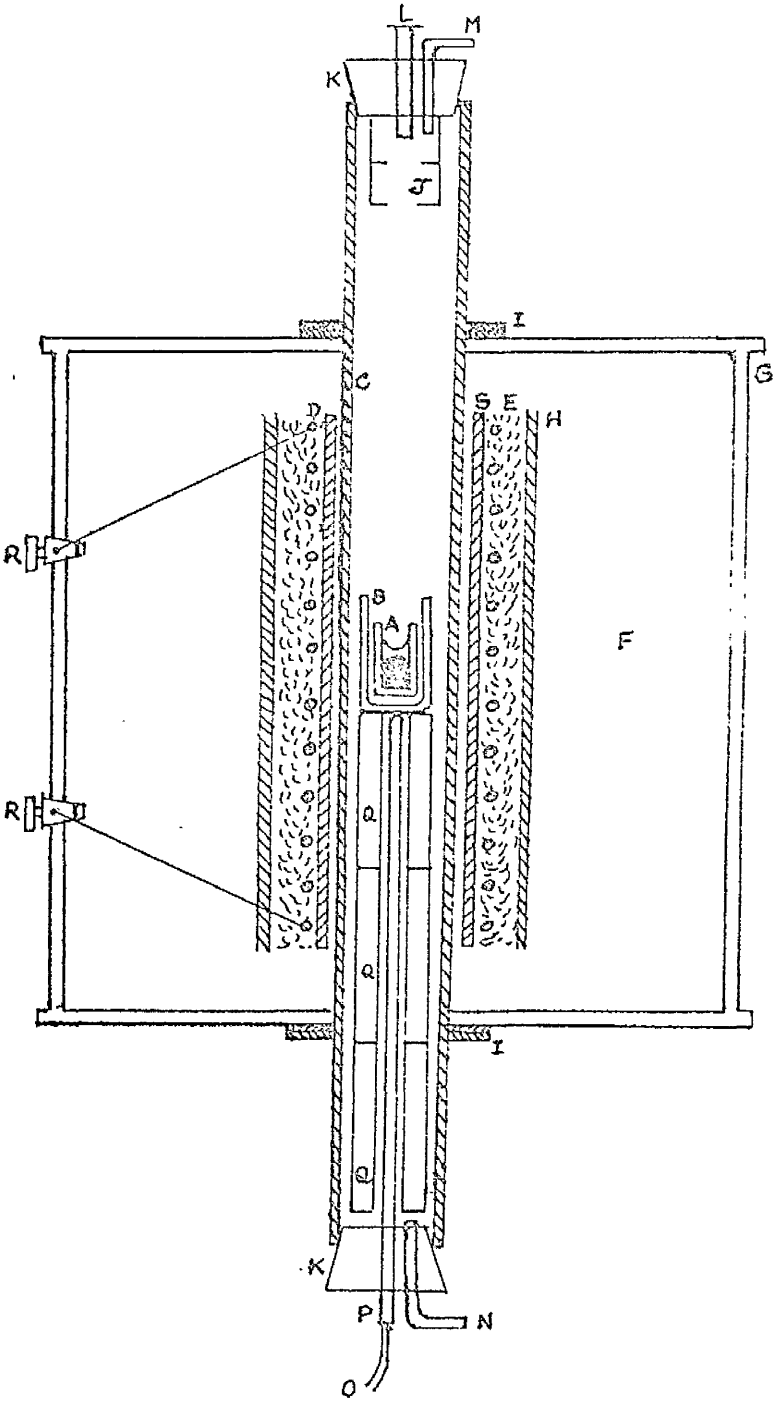


FIG 8 - FURNACE ARRANGEMENT

Temperature measurements were made with the aid of a platinum-13% rhodium platinum thermocouple O protected by mullite sheath F. The tip of the sheath touches the graphite crucible B and was also in the hot zone. The accuracy of this method of temperature measurement has been checked by suspending another platinum-13% rhodium platinum thermocouple inside the crucible. This showed that there was only a temperature difference of 1°C between the two couples and hence was considered quite reliable. This was also evident from the hot-zone chart.

The thermocouple was standardised frequently against the melting point of gold (1063°C). On every occasion it was found that the gold wire tied across the couple melted 2°C higher than the actual melting point of gold, as recorded by the Cambridge portable potentiometer.

The furnace which operates at 1550°C was found to have a hot zone of about 2", along which the temperature did not vary by ± 5°C. The furnace took about 5 hours to attain this operating temperature. The power input to the furnace was manually operated using a sensitive 16 amp variac. The furnace tube being insulated by asbestos cords I at both ends, the temperature could be maintained at 1550 ± 5°C for long periods with only occasional attention. No water cooling arrangement was found necessary, for, the mullite tube was cold at both ends. Whether the molten slag covered up completely the liquid metal during a run could be observed through the

window L at the top fitted to the bung K. This bung was protected from heat by radiation shields J. The melts were carried out in argon atmosphere, the gas from the commercial cylinder being dried by passage through a midgala bulb containing 'anhydrone' (magnesium perchlorate). The gas entered the furnace from the top through the glass tube M and bubbled at a slow rate through a beaker containing water, passing through tube N at the bottom.

(4) FURNACE OPERATION

From the experience gained in earlier runs, the following procedure was found to be satisfactory in establishing equilibrium.-

50 g of Armco iron were made into two pellets and were charged into the magnesia crucible with 25 (or 50) mg sulphur sandwiched between the pellets to give 0·05 (or 0·10)% sulphur in the metal. This crucible was placed inside the graphite crucible and the crucible assembly inserted into the hot zone of the furnace as shown in Fig. 8. The argon supply was then connected to the furnace and the gas was bubbled quickly for the first 10 minutes to purge out all air inside the furnace. The flow rate was slowed down, the power supply was put on and the furnace slowly heated with a current of 10 amps in the beginning. When the temperature reached about 300 or 400°C, the current was increased to 14 amps and maintained at this input till the temperature reached 1550°C. Iron usually melted at a temperature below 1535°C, say about 1530°C, due to the presence of sulphur. In the mean time, the slag was mixed up and kept ready.

The slag consisted of 15 g of homogeneous mixture of a master slag in major portion and varying amounts of Fe_2O_3 and CaS. The master slag for a majority of runs was lime/alumina, while in the rest of the melts lime/silica and lime/alumina/silica were used. There was always considerable loss of Fe_2O_3 due to reduction and sulphur due to oxidation and absorption in the crucible. The amounts of Fe_2O_3 and CaS for the runs were therefore decided by experience only. Usually the slag sulphur was adjusted to a value between 1 and 2%.

Once the temperature was stabilised at 1550°C, the gas flow was increased and it was reversed by disconnecting the supply at the top and connecting at the bottom tube N. This procedure before slag addition kept the oxidation of sulphur from the slag to a minimum. The slag was now added directly into the magnesia crucible in three instalments using a steel tube of 1/4" diameter. After each addition of slag, the bung was closed and sufficient time was allowed to melt the slag which was observed through the window L before subsequent addition was made. The argon supply was then disconnected at N and connected at M so that it flows downwards and the flow rate was reduced. Throughout the run, care was taken to see that the slag covered the metal fully.

The evidence is that the rate of attainment of sulphur equilibrium is very rapid under these conditions. Thus, Bardenheuer and Geller[22] equilibrated their melts with iron-oxide slags for only

10 minutes, while the equilibrium time of Chipman et al varied. For example, the tests of Rocca, Grant and Chipman[67] indicated that sulphur equilibrium is attained in 30 minutes, while Bishop, Grant and Chipman[66] allowed about 45 to 60 minutes. According to Gasanov and Shalimov[68], sulphur equilibrium is attained in a much shorter time, nearly 3 minutes. The present work leads to the conclusion that slag-metal sulphur distribution is very rapid indeed and reached definitely in 1 hour. This conclusion is based upon the results of heats numbers 12 and 15, and 13 and 14 which gave nearly the same value of the distribution coefficient for 1 h and 2 h equilibration times respectively for the same 50 : 50 lime/alumina slag containing nearly the same iron oxide content, but with different metal sulphurs. However, for melts 21 to 62, about 1.1/4 h was allowed.

The question of stirring on the rate of attainment of equilibrium was considered, but no stirring device was incorporated in the present work for two reasons. First of all, the work of Hatch and Chipman[22] in carbon crucibles showed that increasing the stirring speed from 100 r.p.m. to 500 r.p.m. did not greatly improve the rate of attainment of equilibrium. Secondly, sulphur equilibrium in the absence of carbon is already very rapid.

The conventional sampling methods, viz., using an iron rod to sample the slag and a silica tube for sampling the metal, have been adopted in melts 1 to 20. This has been discarded in later runs,

because it was not entirely satisfactory for the following reason. When the same melt was repeated using the same slag composition, the distribution ratio so obtained differed. This is explicable on the basis of delay in sampling, and oxidation of slag and metal during sampling. For a complete analysis about 1.5 g of slag was required. This involved withdrawing slag samples three times from the furnace during which time the remaining slag in the furnace and sulphur in the metal (which was only partly covered with slag now) are likely to oxidise. Hence, a different procedure was looked for. This involved quickly freezing the melt increasing the flow rate of argon after the power was switched off. By this procedure the slag and metal were always solid in about 5 minutes and were kept out of contact with air. In view of the negligible temperature effect on sulphur equilibrium as confirmed by various workers, it is most unlikely that any appreciable shift of equilibrium occurred during cooling down. This procedure has been used previously by Taylor and Stobo[29] and has been adopted here in melts 21 to 62. As will be seen later, this method gave very satisfactory results.

The magnesia crucible was found to be satisfactory for lime/alumina and lime/alumina/silica slags but was found to be not satisfactory for lime/silica slags used in runs 20A to 31B. In these cases the crucible withstood the corrosive action of slag during the run but after the run the crucible was found to be cracked and the slag was

contaminated with fine particles of magnesia from the crucible. It was decided therefore to sample slag and metal with greatest care quickly. However, the silicate slag could not be sampled with the aid of iron rod. This should be explicable on the basis of metal/slag contact angle relationship. The lime/silica slag seems to have a very high contact angle with solid iron so that the latter is not wetted by the slag, whereas in the case of lime/alumina slag and iron, the contact angle has a reasonable value and so can be sampled. Attempts were therefore made to sample the slag with an iron rod having few notches at the end. These were also unsuccessful.

The slag/liquidiron/crucible contact angle relationships have been indicated by Bell [7] who studied the equilibrium between molten iron and FeO-MnO-SiO_2 slags using magnesia and silica crucibles. It has been shown that such slags have low contact angle with respect to silica and magnesia and high angle with respect to liquid iron. The same observation has been made as regards contact angle between metal, magnesia crucible and slags used in this work from an examination of the layer of the slag and metal after each run. The layers of slag and metal are shown in Fig. 8. It appears that lime/silica slags have lower contact angles with magnesia than have lime/alumina slags.

(5) EXPERIMENTAL DIFFICULTIES

(a) Calcium Sulphide Crucibles.-

The difficulties that were encountered in slag/metal sulphur distribution work using slip cast calcium sulphide crucibles have already been discussed and the possible reason for their failure during run was also indicated.

(b) Magnesia Crucibles.-

It has been shown that magnesia crucibles hold molten iron, and lime/alumina, lime/alumina/silica and lime/iron oxide/silica slags respectively, the last slags being used in the preliminary runs (1 - 8). The limitation to silicate study and the sampling difficulties encountered have been mentioned. Even with lime/alumina slags, in some cases where the crucible has been fired to lower temperature, it was found soaked with the slag and the slag did not fully cover the metal. Such runs were repeated using dense and translucent magnesia crucibles.

(c) Segregation.

Sulphur is notorious for segregation. In order to study this aspect the metal buttons in many runs were turned in layers using a lathe and at least four analyses, two from the top and two from the bottom portion of the frozen metal were made. The results indicated that with high sulphurs in the metal, segregation occurred as found from the difference in analyses. Such runs had to be repeated. The results of some of the repeated runs showed that segregation was far less

than the same original run. However, with low sulphur in the metal, segregation was nil or almost insignificant. The metal sulphur analyses reported in this work refer to an average value of the top and bottom portion of the metal button, care thus being taken to reject cases where segregation occurred and to repeat them.

(d) Analytical Difficulties.

(i) Lime and Magnesia in Slag.

The recent EDTA method has been used for the estimation of lime and magnesia in slags. The end points during the titrations are detectable only in good daylight and for this reason the titrations had to be carried out in morning hours on bright days. Attempts to carry out the titrations in dull day light during evening hours have been unsatisfactory. Moreover, in cases where the magnesia content of the slag was high, viz., runs 40, 41, 43 and 49, the combined titration for lime and magnesia did not give proper end point. However, lime estimation could be successfully carried out in such slags.

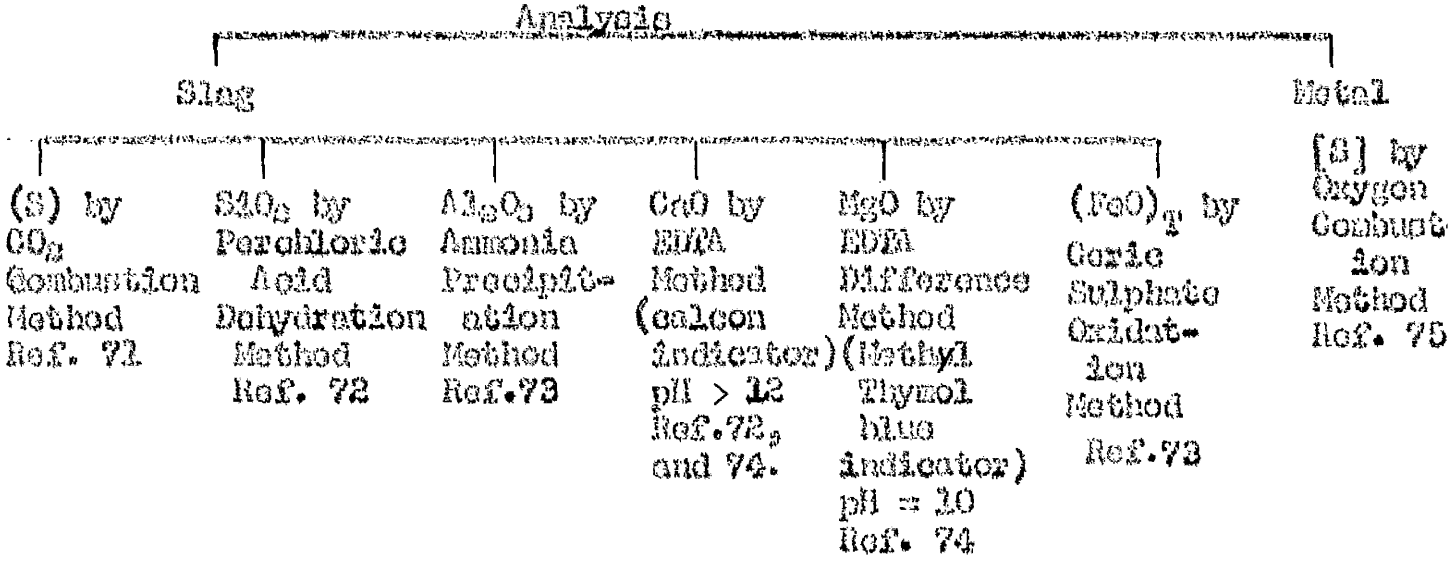
(ii) Sulphur Analysis in Slag.

For some slags, the sulphur analysis by the method of Flinchan and Richardson[71] caused difficulty in that even after three hours, the analysis was still incomplete. This is the case with ternary alumino-silicate slags. The use of a pinch of sodium carbonate as flux, however, reduced the time considerably and was always added.

(6) Analysis of Slag and Metal.

The slag sample was analysed for sulphur, lime, magnesia, alumina, total ferrous oxide and silica, while the metal has been analysed for sulphur. No attempt was made to analyse the oxygen in the metal because it was considered too low and errors involving the use of standard vacuum fusion technique are great. The accuracy of the vacuum fusion method is considered to be ± 0.002%.

The general plan for the analysis of slag and metal is given below.



GENERAL PLAN OF SLAG ANALYSIS

Slag:-

Preparation of Slag for Analysis:-

After freezing in the furnace, the lime/alumina or lime/alumina/silica slags were usually obtained as a button while lime/silica slags were found as powder contaminated with magnesia particles from the crucible. This behaviour of lime silica slags is believed

to be due to the formation of dicalcium silicate.

In the case of lime/alumina or lime/alumina/silica slags, the middle portion of the slag free from any crucible contamination was taken out by breaking the crucible. The slag was then crushed in a percussion mortar with a single blow, transferred to a paper and the coarse particles were separated from the fines by vibrating the paper (i.e. by a method similr to tabling). The coarse slag was transferred to the mortar and the procedure was repeated. In this way, sufficient care was taken to prevent oxidation of the sulphur during the impact by removing the fines as they were formed. The slag was then spread out on a paper and any included iron particles were completely removed by means of a small hand magnet. It has been found that the magnetic particles included in the slag were negligible, and so further magnetic treatment was considered unnecessary.

The slag was then ground in a mechanical grinder for 1 to 2 minutes. Care was taken to minimize oxidation of sulphur as far as possible. It was then stored in a corked specimen tube. For a complete analysis, about 1·5 g. of slag was required.

General Discussion of Slag Analysis.-

Of the various methods available for the estimation of sulphur, viz., the gravimetric method involving precipitation as barium sulphate, the evolution method estimating the liberated hydrogen sulphide, the oxygen combustion method where sulphur is estimated

an sulphur dioxide and the carbon dioxide combustion method where, again, sulphur is oxidised to the dioxide, the last is quick and reasonably accurate and hence is conveniently adopted. This method has been adopted by Fincham and Richardson[73]. No sulphur trioxide is formed and the accuracy of this method is claimed to be < ± 2%. This has been confirmed in the present work using a standard slag of known sulphur content. The use of sodium carbonate as flux was found advantageous in that it decreased considerably the time of assay, although according to Fincham and Richardson a flux is not absolutely essential.

Ethylene diamine tetra acetic acid has been developed as a versatile reagent for the estimation of lime and magnesia by complexometric titration and also for the determination of a variety of other metal ions[76,77]. By a proper control of titration conditions, this method is very accurate and gives quick results compared to the conventional method involving double separation of calcium and magnesium. This method has been applied to silicious materials[78], coal ash deposits[79], and recently to slags[72,74] with some modification because of the interference of aluminium and ferric iron. The titration depends on the formation of EDTA - metal complex from an indicator-metal complex and the pH of the solution is an important factor. Lime is estimated using 'calcon' (Eriochrome Blue Black R) indicator at a pH of over 12 when magnesium is precipitated

as the hydroxide, combined lime and magnesia are estimated at pH 10 using 'methyl thymol blue' as indicator. Complex formation does not take place instantaneously with magnesium and hence it is advisable to carry out the titration slowly[76] near the end point of during the estimation of combined lime and magnesia. Where necessary, triethanol amine was used as a masking agent for aluminium and iron (the latter even in the slightest trace is harmful)[76] and before titration it was necessary to see that the solution did not contain too high a concentration of ammonium ions[76].

Several other methods have been tried for the removal of iron before titration of lime and magnesia during the analysis of the slag. These include the precipitation of iron as hydroxide, reduction of ferric iron to ferrous iron by ascorbic acid and subsequently complexing with sodium cyanide, and lastly solvent extraction with acetyl acetone. Of these, the last method gave slightly lower values for calcium and magnesium, compared with the first two methods which agreed very well with the method using triethanolamine.

The new method for calcium and magnesium has been checked using a standard slag (British chemical standards - No. 171/1 Basic slag) which contains lime, magnesia, iron oxide, alumina, silica, and phosphorus pentoxide along with other minor constituents. After removal of the phosphate ions by a solvent extraction procedure described by Welcher[77], the EDTA method gave only an error of about 0.25% for lime as well as lime and magnesia. This procedure involves removal

of phosphate ions by converting to the heteropolycomplex with sodium molybdate and extracting this complex with n-butanol-chloroform mixture. Thus the EDTA method has been found to be very useful for lime/silica, lime/alumina, lime/alumina/silica slags (containing magnesia) used in the present investigation. Although EDTA is considered a primary standard, its strength was occasionally checked with standard calcium chloride solution or suitable mixtures of standard calcium chloride and magnesium sulphate solutions and the standardisation factor was used for calculating the percentages of lime and magnesia.

Oxidation by ceric sulphate in preference to dichromate has been found to be excellent for the estimation of total iron oxide in small quantities especially when the solution contains hydrochloric, nitric and perchloric acids[70]. Ferroin (ortho phenanthroline ferrous sulphate) is used as indicator. The single dehydration using perchloric acid gave reliable values for silica. For the estimation of alumina, the conventional ammonia precipitation method was found satisfactory as it dispenses with the use of too many stock solutions.

Sulphur

0.2 g of the slag was weighed into a small combustion boat. A pinch of sodium carbonate was added and the boat was inserted into the hot zone of the horizontal platinum furnace maintained between 1400 - 1450°C. This furnace was built specifically for the analysis of

sulphur in the slag and the metal. The sulphur in the slag was oxidised to sulphur dioxide by a constant flow of carbon dioxide (250 cc per minute) and estimated by absorbing in acidulated water contained in two flasks and continuous titration with iodate-iodide solution using starch as the indicator.

The reaction for sulphide slags is

$$(S)_{\text{slag}} + 3O_2 = (O) + 3O + 3O_2 \quad \ldots\ldots\ldots (25)$$

The iodate-iodide standard solution was prepared as follows:- 1.112 g of potassium iodate, 10.6 g of potassium iodide, and 1 g of potassium hydroxide were dissolved in 500 ml of water. This was diluted 10 times.

Hence, (%S) in the slag = $\frac{\text{titre value}}{10}$ on 0.1 g sample

Silica

The silica in slags was estimated by the procedure described by Clarke[70]. A known weight of the slag was dissolved in 1 : 1 hydrochloric acid by digestion over a hot plate till all gritty particles disappear and treated with a few drops of nitric acid to oxidize all iron to the ferric state. The contents were dehydrated by fuming with A.R. perchloric acid (40 ml) for 15 - 20 minutes, diluted and the precipitated silica treated in the usual way in a pulp pad, hydrofluorizing the silica in the end of the determination to give the weight of pure silica. With alumino silicate slags, slow heating was required as there is a tendency for the formation of insoluble aluminium perchlorate.

Alumina

Alumina was determined as the combined oxide. The filtrate from the above estimation was treated with 1 + 1 ammonia in presence of ammonium chloride till just alkaline using methyl red indicator. The combined hydroxide precipitate was filtered, dried, ignited and weighed as $Fe_2O_3 + Al_2O_3$.

Errors in this estimation are due to the amphoteric character of hydrous aluminium oxide and the tendency of the precipitate to pass through the filter, when hot water, instead of ammonium chloride, is used as the wash liquid.

Total Lime

Because of the interference of ammonium ions in the estimation of combined lime and magnesia in the filtrate from the above estimation, the lime and magnesia were determined in a separate sample.

0·5 g of the slag was dissolved in 1 + 1 hydrochloric acid containing nitric acid and made up to a known volume (500 ml). A suitable aliquot, say 25 ml, was first neutralised with 5 N sodium hydroxide to bring the pH above 12. 10 ml of 33% methanol amine was added to complex iron and aluminium. The contents were diluted to 200 ml and titrated with standard EDTA (M/50) using calcon as indicator (2 ml, 0·2 % solution in triethanolamine). The end point, detectable very easily in good day light, is marked by the disappearance of all traces of red colour and the appearance of a permanent (sky blue) colour.

1 ml of std EDTA = 1% lime on 0·1 g sample.

This estimation gives the total calcium (i.e. calcium present as oxide and sulphide in the slag).

Total Lime and Magnesia

25 ml aliquot from the above stock solution was neutralised using 5N sodium hydroxide and treated with 8 ml of ammonium chloride - ammonium hydroxide buffer of pH 10. It was then treated with 10 ml of 33% triethanolamine, diluted to 200 ml, and titrated with standard EDTA using methyl thymol blue (2ml, 0·1% solution in trichhanolamine) as indicator. The end point is marked by the disappearance of all traces of blue colour and the appearance of a permanent red colour, the titration being carried out in good daylight.

The difference between this titre value and the titre value for total lime gives the volume of EDTA consumed by magnesia.

1 ml of std. EDTA = 0·71% MgO on 0·1 g sample

The buffer, used in the titration, was prepared as follows:-

67·5 g of ammonium chloride and 570 ml of ammonium hydroxide (Sp. gr. = 0·88) were dissolved in about 250 ml water. 0·931 g of EDTA and 0·616 g of $MgSO_4.7H_2O$ were dissolved in about 50 to 60 ml water. The two solutions were mixed and diluted to a litre.

Total Ferrous Oxide

The iron oxide content of the slag is so small that it was advisable to determine it in a separate sample. A known weight (0·2g) of the slag was dissolved in dil hydrochloric acid and the solution was made 5 to 6 N withconc hydrochloric acid. The ferric iron was reduced with stannous chloride (about 7% solution in hydrochloric acid) in the usual way. For efficient reduction, the solution should not be more than 25 ml. The excess stannous chloride was destroyed by adding 15 ml of mercuric chloride solution and allowed to stand for 1 to 2 minutes till a faint white silky precipitate appeared. The solution was diluted to 200 ml with 2·5 % sulphuric acid and titrated with $N/_{100}$ ceric sulphate using a drop of 'ferroin' as indicator. The end point is the first sharp change of red colour.

The ceric sulphate solution was prepared by dissolving commercial ceric ammonium sulphate in N sulphuric acid, it was filtered and standardized against A R iron wire. The indicator was prepared by dissolving 1·485 g of orthophenanthrolene monohydrate in 100 ml of 0·025 M ferrous sulphate, prepared by dissolving 0·695 g of crystalline ferrous sulphate in 100 ml water.

METAL

Sulphur

The metal was obtained as a button and uniform turnings were turned out in a lathe from the top and bottom of the sample for

sulphur analysis. The average of the two values, which did not differ significantly, was taken to represent metal sulphur.

Oxygen was passed over 0·5 g of the metal turnings contained in a boat placed in the hot zone of the horizontal platinum furnace maintained at 1300°C. The liberated sulphur dioxide was absorbed in acidulated water and titrated with iodate-iodide solution using starch as the indicator in the usual way. One complete assay requires about 30 minutes.

The method was checked with a standard cast iron (British Chemical Standards No. 247/2, white cast iron) which was found to be close to their assay within an error of 1%.

(7) An estimate of the accuracies of the analyses of slag and metal

Slag		Metal	
Sulphur	± 1%	Sulphur	± 1%
Lime	± 0·1%		
Magnesia	± 0·1%		
Iron oxide	± 0·5%		
Alumina	± 0·5%		
Silica	± 1%		

TABLE 4 - SHOWING ESTIMATED ACCURACY OF ANALYSES.

CHAPTER IV

RESULTS

RESULTS

When the work was first suggested, it was the intention to investigate slag-metal distribution of sulphur making use of calcium sulphide crucibles. By this means, it was hoped, true lime activity values could be obtained. This plan, however, met with little success owing to constant failure of the slip-cast calcium sulphide crucibles during melts. It was noted that this failure was due to the slag soaking into the crucible or the crucible getting cracked during melts, before any attempt at sampling was made. Attention was therefore focussed on magnesia crucibles.

Preliminary experiments conducted with magnesia crucibles revealed that these could be used to study sulphur distribution between lime-alumina slags and molten iron. Since the partition of sulphur between metal and slag depends on the oxide ion activity or, in particular, the activity of lime in the slag and also on the oxygen potential of the system as reflected in the ferrous oxide content of the slag, numerous melts were made using lime-alumina slags with varying iron oxide contents. This attempt proved very successful. A few lime-silica slags were tried afterwards. These melts were not as successful as those using lime-alumina slags due to the formation of fluffy dicalcium silicate which included fine particles of magnesia from the crucible after the run. These could be detected by a lens. Considerable difficulty was found in separating the

the magnesia particles from the slag before analysis. The magnesia analyses in melts 291 to 310 using these slags were of the order of 6 - 8% (excepting melt 30 where MgO = 12%). Examination of the $CaO-MgO-Al_2O_3$ and $CaO-MgO-SiO_2$ diagrams, Figs. 6 and 7, revealed that the solubility of magnesia in lime-alumina slag of basic composition 55% lime is about 7% at 1550°C and the solubility in lime-silica slag of similar composition is about 10%. It is therefore considered that the distribution ratios obtained for lime-silica slags are approximately correct. These have also been included in the table. In runs 36 to 39, about 5% silica was added to the lime-alumina slags and in this way a study of the effect of low percentages of silica in $CaO-Al_2O_3-MgO-SiO_2$ slags was attempted. This attempt also proved successful.

In order to make reference easier, it is proposed to report the experimental results in three sections.

1. Lime-magnesia-iron oxide-alumina slags and metal.
2. Lime-magnesia-iron oxide-silica slags and metal.
3. Lime-magnesia-iron oxide-alumina-silica slags and metal.

The results are presented in tabular form in Tables 5, 6 and 7, containing chemical analyses of all the melts. No detailed study of the effect of temperature on sulphur partition between slag and metal was made during the present work and all the experiments were carried out at a temperature of 1550° C. The melt numbers missing from the tables refer to those melts where attempts have been

TABLE 5 - DISTRIBUTION OF SULPHUR BETWEEN LIME-MAGNESIA-IRON OXIDE-ALUMINA SLAGS AND MOLTEN IRON AT 1550°C.

Melt No.	$(\%CaO)_s$	$(\%MgO)$	$(\%FeO)_t$	$(\%Al_2O_3)$	$(\%S)$	$[\%S]$	$[S]/[\%S]$	$[Fe]$	$(\%b)/[a_c]$
21	51·73	6·27	0·76	40·67	0·89	0·0329	27·15	0·9979	27·20
22	40·75	9·39	0·686	49·39	0·668	0·1322	5·05	0·9926	5·09
23	45·60	8·90	0·659	44·44	0·8035	0·0542	14·86	0·9965	14·91
24	41·05	8·76	1·183	48·98	0·1595	0·0644	2·48	0·9959	2·49
25	41·35	6·19	0·33	51·50	1·264	0·0981	12·88	0·9936	12·97
26	43·25	8·92	0·53	47·21	1·285	0·1054	12·20	0·9931	12·28
27	50·40	6·16	0·788	40·25	3·29	0·112	29·4	0·9926	29·65
28	46·6	7·16	0·553	45	1·415	0·0711	19·9	0·9954	20
40	30·43	38·25	1·254	29·7	0·7125	0·032	22·43	0·9979	22·5
41	30·20	34·34	1·13	33·46	0·755	0·0671	11·25	0·9956	11·3
42	40·25	10·87	1·618	47·05	0·4217	0·1355	3·15	0·9913	3·18

TABLE 5 (CONT'D) - DISTRIBUTION OF SULFUR BETWEEN LIME-MAGNESIA-IRON OXIDE-ALUMINA SLAGS AND MOLTEN IRON AT 1550°C

Melt No.	$(\%CaO)_s$	$(\%MgO)$	$(\%FeO)_s$	$(\%Al_2O_3)$	$(\%S)$	$[\%S]$	$(\%S)/[\%S]$	$[Fs]$	$(\%S)/[a_s]$
43	32.7	41.26	1.25	21.91	5.77	0.0841	68.6	0.9933	69.1
44	44.9	10.7	1.02	42.84	1.08	0.1305	8.28	0.9915	8.35
45	41.6	8.42	0.631	48.5	1.262	0.174	7.48	0.9868	7.52
46	45.25	12.95	0.863	40.06	1.765	0.053	33.3	0.9965	33.4
47	40.4	13.45	1.185	44.17	1.506	0.231	6.92	0.9851	7.02
48	42.8	13.87	1.01	41.76	1.123	0.1045	10.75	0.9933	10.83
50	38	13.08	3.46	45.01	0.868	0.5155	1.72	0.9874	1.78
51	42.75	13.1	3.33	40.27	1.092	0.313	3.495	0.9802	3.56
52	46.7	11.8	4.21	36.61	1.363	0.2565	5.315	0.9835	5.4
53	38.6	12.2	2.34	46.28	1.15	0.4339	2.65	0.9725	2.73
54	42.7	12.31	3.1	41.25	1.266	0.386	3.265	0.9754	3.34

TABLE 5 (CONT'D) - DISTRIBUTION OF SULPHUR BETWEEN LIME-MAGNESIA-IRON OXIDE-ALUMINA SLAGS AND MOLTEN IRON AT 1550°C

Melt No.	$(\%CaO)_s$	$(\%MgO)$	$(\%FeO)_t$	$(\%Al_2O_3)$	$(\%S)$	$[\%S]$	$(\%S)/[\%S]$	$[Fe]$	$(\%S)/[a_s]$
55	46·25	12·08	3·675	36·85	1·88	0·343	5·48	0·9762	5·6
55	40·5	12·84	5·55 4·6*	40·67	0·8815	0·3375	2·64	0·9786	2·7
57	43·25	12·39	7·61 6·11*	36·39	0·729	0·2255	3·23	0·9856	3·27
58	38·95	10·23	1·038	49·28	1·044	0·2272	4·59	0·9858	4·65
59	44·9	10·16	3·435	40·97	1·043	0·238	4·38	0·9854	4·44
60	39·5	11·54	0·988	47·26	1·438	0·239	6·02	0·9852	6·12
61	47·6	9·1	2·195	40·35	1·495	0·1854	8·06	0·9886	8·16
62	38·45	11·86	1·43	47·72	1·0865	0·2865	3·79	0·9823	3·86

* True ferrous oxide in the slag

TABLE 6 - DISTRIBUTION OF SULPHUR BETWEEN LIME-MAGNESIA-IRON OXIDE-SILICA SLAGS AND LIQUID IRON AT 1550°C.

Melt No	$(\%CaO)_t$	$(\%MgO)$	$(\%FeO)_t$	$(\%SiO_2)$	$(\%S)$	$[\%S]$	$(\%S)/[\%S]$	[Fs]	$(\%S)/[as]$
29A	53·6	5·9	0·574	39·19	0·437	0·161	2·71	0·99	2·73
$29S_1$	51·75	5·98	0·644	40·85	0·78	0·107	7·3	0·9933	7·35
$29S_2$	51·75	5·98	0·644	40·85	0·553	0·107	5·17	0·9933	5·2
30	49·3	12·1	0·978	35·65	1·42	0·1175	12·1	0·9926	12·19
31A	51·5	8·25	1·334	37·6	0·736	0·1885	3·9	0·9886	3·95
31B	51·8	7·57	1·297	38·6	0·52	0·31	1·65	0·981	1·68

Remarks.

MELT 29A. Could not sample and hence cooled in the furnace in an atmosphere of argon.

MELT $29S_1$. Slag was sampled, but metal cooled in the furnace. Sulphur analysis carried out in sampled slag, but slag cooled in the furnace used for the assay of other constituents.

MELT $29S_2$. Same as $29S_1$, all analyses being carried out in slag and metal cooled in the furnace.

MELT 30. Sulphur analysis carried out in sampled slag, but the slag cooled in the furnace was used for the assay of remaining constituents.

MELTS 31A, 31B. Slag and metal cooled in the furnace.

TABLE 7 - DISTRIBUTION OF SULFUR BETWEEN LIME-MAGNESIA-IRON OXIDE-ALUMINA-SILICA SLAGS AND MOLTEN IRON AT 1550°C

Melt No.	$(\%CaO)_t$	(%MgO)	$(\%FeO)_t$	($\%Al_2O_3$)	($\%SiO_2$)	(%S)	[%S]	$(\%S)/[\%S]$	[fs]	$(\%S)/[a$
34	42•6	8•52	0•835	43•14	4•25	1•314	0•0928	14•16	0•9842	14•25
35	40•6	7•1	0•723	46•68	4•36	1•2125	0•1152	10•51	0•9926	10•6
36	37•72	10•18	0•676	46•82	4•34	1•107	0•1625	6•82	0•99	6•88
37	46•25	6•43	1•045	38•78	4•2	2•585	0•155	16•5	0•9904	16•68
38	38•9	11•07	0•647	44•86	4•53	1•764	0•1401	12•72	0•9913	12•84
39	36•9	11•42	0•915	45•24	4•675	1•695	0•229	7•4	0•9865	7•5

made to study the equilibrium time necessary for a run and those considered unsatisfactory for analysis due to high magnesia contents.

In the first column, the total lime content of the slag, $(CaO)_t$ is given. i.e. total calcium ions converted to oxide. This is the sum of the calcium ions present as oxide and sulphide. From the experience gained with earlier slags where both total iron and ferrous oxide content of the slag have been analysed, it was noted that the amount of ferric oxide present was negligibly small in slags low in iron oxide. Hence in the majority of runs made in this investigation, the total iron-oxide content of the slag has been analysed and expressed as 'total iron oxide', $(FeO)_t$. However, in runs 56 and 57, the true ferrous oxide content of the slag have also been analysed in an atmosphere of carbon dioxide. These are also included in Table 5.

The analyses of alumina has been carried out for some of the earlier melts. These agree very well with the alumina content obtained by difference. For example, in slag 21, the sum of the constituents, taking all the sulphur as calcium sulphide, is $CaO + CaS + MgO + FeO = 50.19 + 1.98 + 6.27 + 0.76 = 59.2\%$. Hence alumina by difference $= 100 - 59.2 = 40.8\%$. The analysed alumina was 40.87%. This indicated that the difference method of computing alumina percentage is applicable to the slags used in this investigation, provided the assessment of all other constituents

is made in equilenbe.

The assumption that all the sulphur exists in the slag as calcium sulphide appears to be valid because lime is the major basic constituent in the slag and the amount of sulphur present in the slag is very small. This contention is supported by a consideration of the cationic radius which decreases in the series CaO, FeO, MgO meaning that MgO is more stable. Moreover, the sulphide ion is more strongly polarized than the oxide ion (because the former is larger) in the vicinity of magnesium ion thereby showing the stability of MgO. The free energy considerations also favour the existence of practically all the sulphur in the slag as calcium sulphide.

viz.

$$(CaO) + \underline{S} = (CaS) + \underline{O} \qquad \Delta G°_{1600\,°C} = 11,740 \text{ cals.}$$

$$(FeO) + \underline{S} = (FeS) + \underline{O} \qquad \Delta G°_{1600\,°C} = 14,800 \text{ cals}$$

$$(MnO) + \underline{S} = (MnS) + \underline{O} \qquad \Delta G°_{1600\,°C} = 17,600 \text{ cals}$$

$$(MgO) + \underline{S} = (MgS) + \underline{O} \qquad \Delta G°_{1600\,°C} = 33,400 \text{ cals}$$

These free energy values also show that magnesia is a poor desulphuriser.

The exact significance of magnesia in desulphurization has not been understood to date, because of lack of accurate data on the activity of oxide and sulphide ions in liquid slags. Moreover

a crucible other than magnesia is required to make the magnesia content of the slag an independent variable and to study the effect of increasing percentages of magnesia. Hardern, Grove and Oelsen[68] could not find any desulphurisation taking place from molten iron containing sulphur by magnesium silicate slags or pure magnesia at sintering temperatures (1700°C), while Maurer and Bischof[104] found no apparent effect of magnesia on desulphurization in the range 0 - 10%. The latter also suggested that higher amounts of magnesia might impair desulphurization to a slight extent. Hatch and Chipman[39] considered MgO to be equivalent to $^2/_3$ CaO on a mol basis in their desulphurizing powers under blast furnace conditions, but Rocca, Grant and Chipman[87] assessed CaO to be 1000 times a better desulphurizer than MgO. From the gas-slag work of Kalyanram et al[39], it is estimated that the main effect of MgO in desulphurization is to increase 'A_{CaO}'. From the present results it appears that MgO at low concentrations has very little effect in increasing the sulphur distribution ratio where as at higher concentrations it definitely increases the distribution coefficient. This can be seen in melts 40, 41 and 43. Thus the role of magnesia is an indirect one in that it neutralises the acid constituents in the slag, releasing lime which aids desulphurization.

The last three columns of the tables give $\frac{(\%S)}{[\%S]} \cdot [f_s]$ and $\frac{(\%S)}{[a_s]}$ values, the last being a better measure of sulphur

distribution than the usual distribution coefficient, $\frac{(\%S)}{[\%S]}$. The activity coefficient of sulphur in the metal, $[f_S]$, has been calculated from the data of Sherman, Elvander and Chipman[6] who observed a linear variation of log f_S with [%S] in the metal for concentrations up to at least 0,5 or 1 weight % sulphur. The relation is given by,

$$\log f_S = e_S [\%S]$$

where e_S is the interaction coefficient (i.e., $e_S = \partial \log f_S / \partial \%S$). e_S is obtainable from the slope of the plot of log f_S v. [%S]. It has a value of -0.0200 at 1550°C and -0.0270 at 1600°C, the former value being suitable to calculate f_S values in this work. $\frac{(\%S)}{[e_S]}$ can now be calculated from $\frac{(\%S)}{[\%S]}$ by division by f_S. It is unfortunate that the existing experimental data in literature seem inadequate to compute $\frac{(a_S)}{[a_S]}$ which could be the best measure of sulphur distribution between slag and metal.

A rough analysis of the results reveals that the distribution ratio increases as the percent lime is increased and it decreases as the iron oxide content is increased.

Lastly, it seems opportune to make some comments on the appearance and nature of the slags after the run. While lime-silica-magnesia-iron oxide slags were fluxy, lime-alumina-magnesia iron oxide slags and lime-alumina-silica-magnesia-iron oxide slags were glassy and opaque in appearance. On grinding in a mortar,

some of them were nearly white in colour while others possessed a yellow colour. Attempts to judge from colour alone the sulphur content of the slag approximately was often found to be misleading, for some slags with higher sulphur content were nearly white in colour and some slags with lower sulphur content possessed a yellow colour. Thus the colour of a lime-alumina-magnesia-iron oxide slag or lime-alumina-silica-magnesia-iron oxide slag seems to be more due to the alumina and iron oxide content rather than the sulphur content.

CHAPTER V

DISCUSSION

D I S C U S S I O N

(1) Discussion of Experimental Results.

Although lime has long been recognized as an effective desulphuriser, it is very well known that oxides other than lime, to a greater or lesser degree, may take part in effecting sulphur removal. Examination of the standard free energy changes for the reactions between sulphur in the metal and each of the basic oxides in the slag, page 89, shows that the desulphurising power of the basic oxides in the slag decreases in the series CaO, FeO, MnO, MgO, the last being least effective in desulphurization.

In view of the part played by oxides other than lime in desulphurization and in view of the ionic nature of liquid slags, the reaction of interest in the distribution of sulphur between molten iron and slag can be conveniently represented in an ionic form as follows.

$$(O^{--}) + \underline{S} = (S^{--}) + \underline{O} \qquad \text{.....(15)}$$

The equilibrium constant for this reaction is given by,

$$K_{15} = \frac{(a_{S^{--}})[a_O]}{(a_{O^{--}})[a_S]}$$

$$= \frac{L_S}{32\,n} \cdot \frac{(\nu_{S^{--}})[a_O]}{[f_S]\,(a_{O^{--}})}$$

where,

L_S is the sulphur distribution coefficient, i.e. $\frac{(\%S)}{[\%S]}$

n is the total number of mols of slag constituents

and, $(\nu_{S^{--}})$ and $[f_S]$ refer to the activity coefficients of sulphide

ions in the slag and sulphur in the metal respectively. For small concentrations of sulphur encountered in the metal, Henrian behaviour can be assumed up to about 0·5 wt % and so,

$$L_S \propto \frac{(a_{O^{--}})}{(\gamma_{O^{--}})[a_O]} .$$

Thus the partition of sulphur between molten slag and iron varies directly as the function $(a_{O^{--}})/(\gamma_{O^{--}})$ for constant $[a_O]$ and inversely as $[a_O]$ for given $(a_{O^{--}})/(\gamma_{O^{--}})$. The former is related to the basicity of the slag and the latter to the iron-oxide content of the slag or metal oxygen content or, more broadly, the oxygen potential of the system. Thus the distribution of sulphur between molten iron and slag depends on slag basicity and also on the oxygen potential of the system. The iron oxide content of the slag is doubly important because, while increasing the basicity of the slag it also increases the oxygen potential controlling the system. This has been noted previously.

Although the part played by low oxygen potential in controlling desulphurization has been realized in the past, it has not been possible to study varying amounts of ferrous oxide in the slag on sulphur partition. This difficulty arose due to the use of carbon crucibles and so the oxygen pressure was fixed at a low value by means of the reaction

$$\underline{C} + \underline{O} = CO_{(g)} \qquad \text{.....(22)}$$

Moreover, as seen earlier, difficulty was encountered in separating the metallic iron which was dispersed in the slag. Again, even if the iron oxide content of the slag is completely freed from any metallic iron, the analytical accuracy is low. Also the analytical accuracy in sulphur assay is far less due to the low concentrations of sulphur encountered in the metal. This, as seen already, is due to the increased activity coefficient of sulphur in presence of carbon and silicon. Another point to consider is the doubtful approach to equilibrium. Interpretation of the results in carbon crucible experiments was therefore restricted to slag basicity only. It will be seen shortly that there is wider scope of interpretation of results in experiments using magnesia crucibles in that basicity as well as oxygen potential can be varied.

(a) Effect of Basicity on Sulphur Partition.

There is as yet no reliable method of assessing the activity of oxide ions in the slag, and so several basicity expressions were developed in the past to correlate the experimental results. It should be pointed out that these basicity expressions, while correlating well with sulphur distribution coefficient within the range of slag compositions studied, may not correlate so well outside the range. For example, Gladroyo[66] mentions the use of four basicity expressions used in industrial practice. They are:-

(i) The 'excess base' expression of Rotch and Chipman[88]

i.e. $(CaO + \frac{2}{3}MgO) - (SiO_2 + Al_2O_3)$ in mols per 100 g slag.

(ii) Bell's Ratio[25]

i.e. $$\frac{\%CaO + \%MgO/2}{\%SiO_2 + \%Al_2O_3/3} = \frac{\%CaO + 0.7\ \%MgO}{0.94(\%SiO_2) + 0.18(\%Al_2O_3)}$$

(iii) 'Russian ratio' (Kulikov expression)[86].

i.e. $$\frac{\%CaO + \alpha\%MgO - 1.75\%S}{\%SiO_2 + 0.6\%Al_2O_3 \quad \%CaO + \alpha\%MgO} = 1.19$$

where $\alpha = \frac{1.64\%SiO_2 - 0.9\%CaO}{\%SiO_2 + 0.9\%MgO}$

(iv) the usual basicity ratio.

i.e. $$\frac{\%CaO + \%MgO}{\%SiO_2 + \%Al_2O_3}$$

Of these the usual basicity ratio seems less satisfactory in that it gives equal prominence to silica and alumina on a weight percent basis in reducing basicity. Moreover, it shows that lime and magnesia are equivalent on a wt % basis. The Russian Ratio is tedious from the point of view of calculation. The 'excess base' and Bell's expression are equally satisfactory, for a good correlation between these two exists for the composition of slags used in this work. The latter, however, is preferred for the following reason. When the distribution ratio was plotted against iron-oxide content for various basicity values, the various Bell's curves were clearly separated, while the various 'excess base' curves were very close to each other and so the former was used.

A comment has been made on the use of alumina in the basicity expression by Kulikov et al[56]. Being amphoteric, its behaviour in slags depends on the other components. In basic slags it will react with basic oxides and so in this case it should be included in total acidic oxides. In acid slags, alumina has basic properties and should therefore be included in the sum of the bases. It should be recalled that a majority of slags used in this investigation contain lime and alumina.

In Fig.9, the distribution coefficient, $\frac{(\%S)}{[\%S]}$ is plotted against mole fraction of iron oxide for various Bell's ratios. It will be seen from the plot that the distribution ratio increases with basicity for constant iron oxide content of the slag and further that iron oxide in small amounts has much greater effect in reducing the distribution coefficient at constant basicity than at higher concentrations. Higher concentrations of iron oxide in the range investigated do not have any significant effect on sulphur partition.

The effect of small amounts of silica on sulphur partition is of interest. In runs 34-39, lime-alumina-silica slags have been used containing about 4-5% silica. It is seen from Fig.9 that the points with a basicity value of 3-4 for such slags lies between the curves for lime alumina slags with the values of 5-6 and 6-7 (with the exception of one point). Further, the points with basicity ratio 4-5 lies between the curves with values of 6-7 and 7-8 for lime-alumina slags. A possible explanation for this anomaly is the

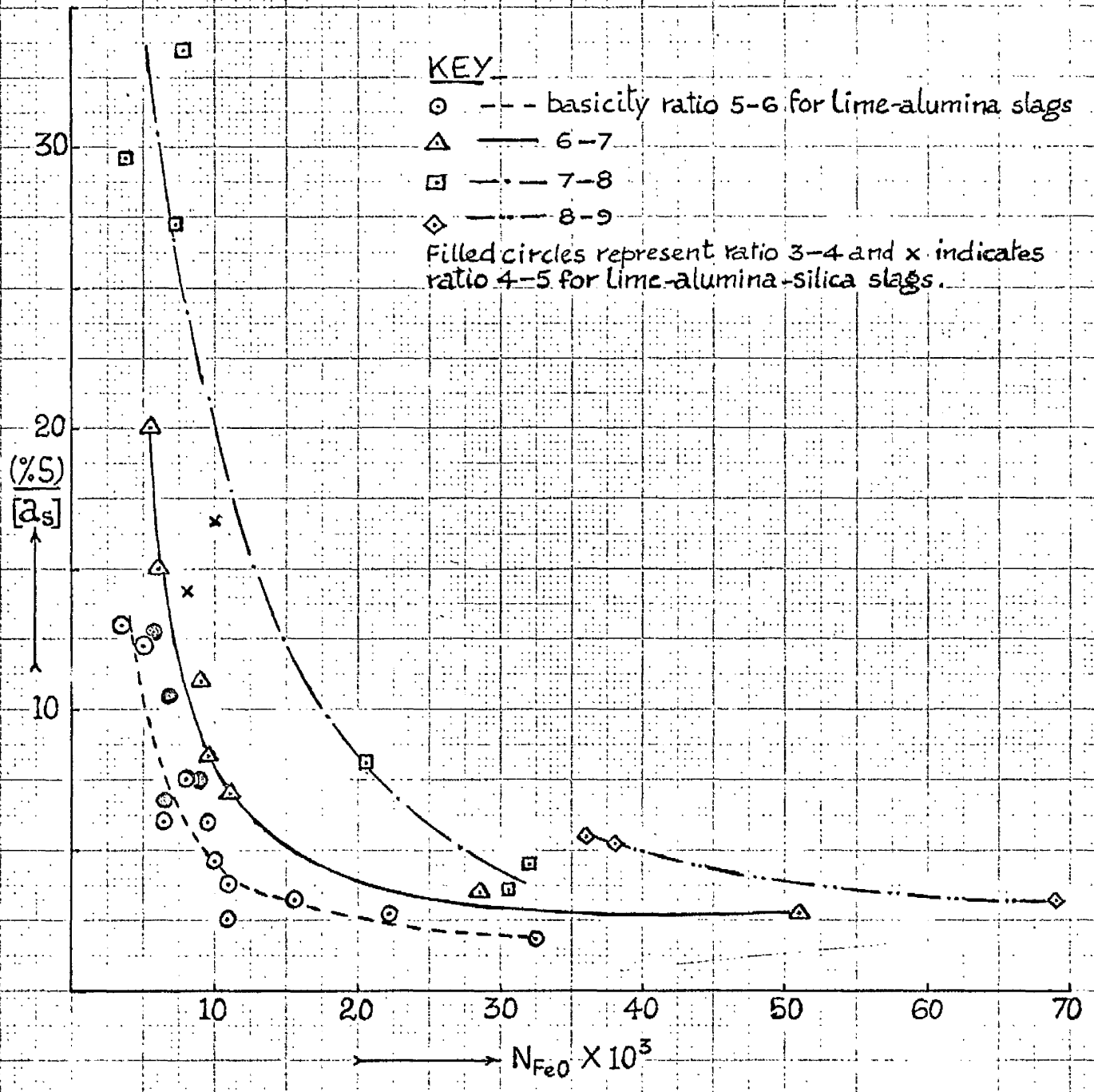


FIG 9 Effect of Basicity (Bell's Ratio) and of iron oxide content of the slag on the equilibrium distribution coefficient of sulphur at 1550°C

fact that the solubility of sulphur in lime-alumina-silica slags is much more than the solubility in lime-alumina slags. Hence ν_S^{m} will be lower for lime-alumina-silica slags than for lime-alumina slags. Therefore at constant iron oxide content of the slag and given lime activity, $(\%S)/[a_a]$ is greater in the case of the former than in the latter. It is also likely that in the range of slag composition the ratio does not apparently correlate well with lime-alumina and lime-alumina-silica slags. Since the ratio was developed from correlation using slags in the system lime-alumina-magnesia-silica with much higher silica contents it would not necessarily correlate well in the range of slag compositions used here.

The data available for comparison are those of Hatch and Chipman[28], and Kulikov et al[27] using carbon crucibles and those of Taylor and Stobo[40] using carbon and alumina crucibles. The results in carbon crucibles are difficult to plot with the present results in Fig. 9 in view of the low percentages of iron oxide. The results of Taylor and Stobo in alumina crucibles contain greater amounts of iron oxide. However, in this case their distribution coefficients are very low. Kulikov et al did not analyse for iron oxide in their melts and even if iron oxide analyses are available for their melts, they are expected to be very low. Further, their distribution values are high, as measured by their 'sulphur absorption power', C^S. However, an attempt was made to plot $(\%S)/[a_S]$ v. N_{FeO} for the

data of Katch and Chipman (making use of their 'second analysis' for iron oxide). This showed that the points can be represented by a straight line (with Hall's ratio 1 : 2) which is parallel and very close to the $\frac{(\%O)}{[\%O]}$ axis.

(b) Activity of Iron Oxide in Slags

The activity of iron oxide in binary, ternary and more complex slags has been the object of numerous investigations, in view of its importance in iron and steel making. The iron oxide activity gives the exact measure of the 'oxidising power' of the slag i.e. the amount of oxygen that the slag is capable of transferring to the liquid steel bath. Iron oxide takes part in various slag-metal reactions and hence is responsible for the removal of Mn, Si, P and C.

The experimental methods adopted to estimate the ferrous oxide activity in the slag has been of two types.

(i) to equilibrate the metal with the slag in question and measure the oxygen content of the metal. Ferrous oxide activity is then given by

$$a_{FeO} = \frac{[\%O]}{[\%O]_{sat}}$$

where, $[\%O]_{sat}$ is the oxygen content of the metal in equilibrium with pure iron oxide slag.

(ii) to equilibrate the slag in iron crucibles with known

partial pressures of hydrogen-steam or CO/CO_2 mixtures. This method is limited to temperatures between 1265 and 1500°C.

The first method has been used by Chipman et al[88,89] and the latter by other investigators[84,90,97].

In view of the very low oxygen content of the melts used in this investigation, it has not been found possible to derive the ferrous oxide activity by method (1). The ferrous oxide activities could, however, be computed from the gas-slag equilibrium studies of sulphur using the concept of sulphide capacity.

Bell and Kalyanram[20] have investigated the sulphur absorption characteristics of lime-alumina slags containing magnesia by the Carter-Macfarlane method[10], i.e. by comparing the sulphide capacity of the slag in question to that of a standard slag of unit lime activity and have derived the lime activity values. As discussed previously, their lime activity is given by

$$A_{CaO} = \frac{(\%S)/A}{(\%S^o)A^o} = \frac{C_S}{C_S^o}$$

where, $A = \frac{P_{S_2}^{1/2}}{P_{O_2}^{1/2}}$ & $C_S = \frac{(\%S)P_{O_2}^{1/2}}{P_{S_2}^{1/2}}$ and the superscript zero refers to the standard slag. (A_{CaO} is used here instead of a_{CaO} to denote lime activity, because this is not the true lime activity). A slag having the composition CaO = 60%, Al_2O_3 = 32.6% and SiO_2 = 7.4% has been chosen as the standard slag possessing unit lime activity. This was found to absorb 2% sulphur from the gas mixture consisting of

$CO/CO_2/SO_2$ and with sulphurising potential $A^o = 307$. This value of sulphurising potential has been calculated from thermodynamic data of gaseous compounds given by Kelley[60] and by Dowing and Richardson[59] for CO. The isoline activity lines drawn for the system $CaO-MgO-Al_2O_3$ at 1500°C is reproduced in Fig.10.

The sulphide capacity of a lime-alumina-magnesia slag can therefore be calculated using the relation,

$$C_S = C_S^o \times A_{CaO}$$

$$= \frac{2}{307} \times A_{CaO} \text{ at } 1500°C,$$

taking lime activity value for any slag under consideration from this ternary diagram.

It can reasonably be assumed that the low iron oxide contents encountered in slags used in the present work have little significant effect on the lime activities and so the same ternary diagram can be used to determine the sulphide capacities of these slags.

The effect of temperature on sulphide capacity requires further examination, as the present investigation has been carried out at 1550°C. The equilibrium constant for the reaction,

$$(CaO) + \tfrac{1}{2}S_2(g) = (CaS) + \tfrac{1}{2}O_2(g) \quad \text{.....(23)}$$

is given by

$$K_{23} = \frac{(a_{CaS})}{(a_{CaO})} \times \frac{p_{O_2}^{1/2}}{p_{S_2}^{1/2}}$$

$$= \frac{C_S(\nu_{CaS})}{32 \cdot n \cdot (a_{CaO})}$$

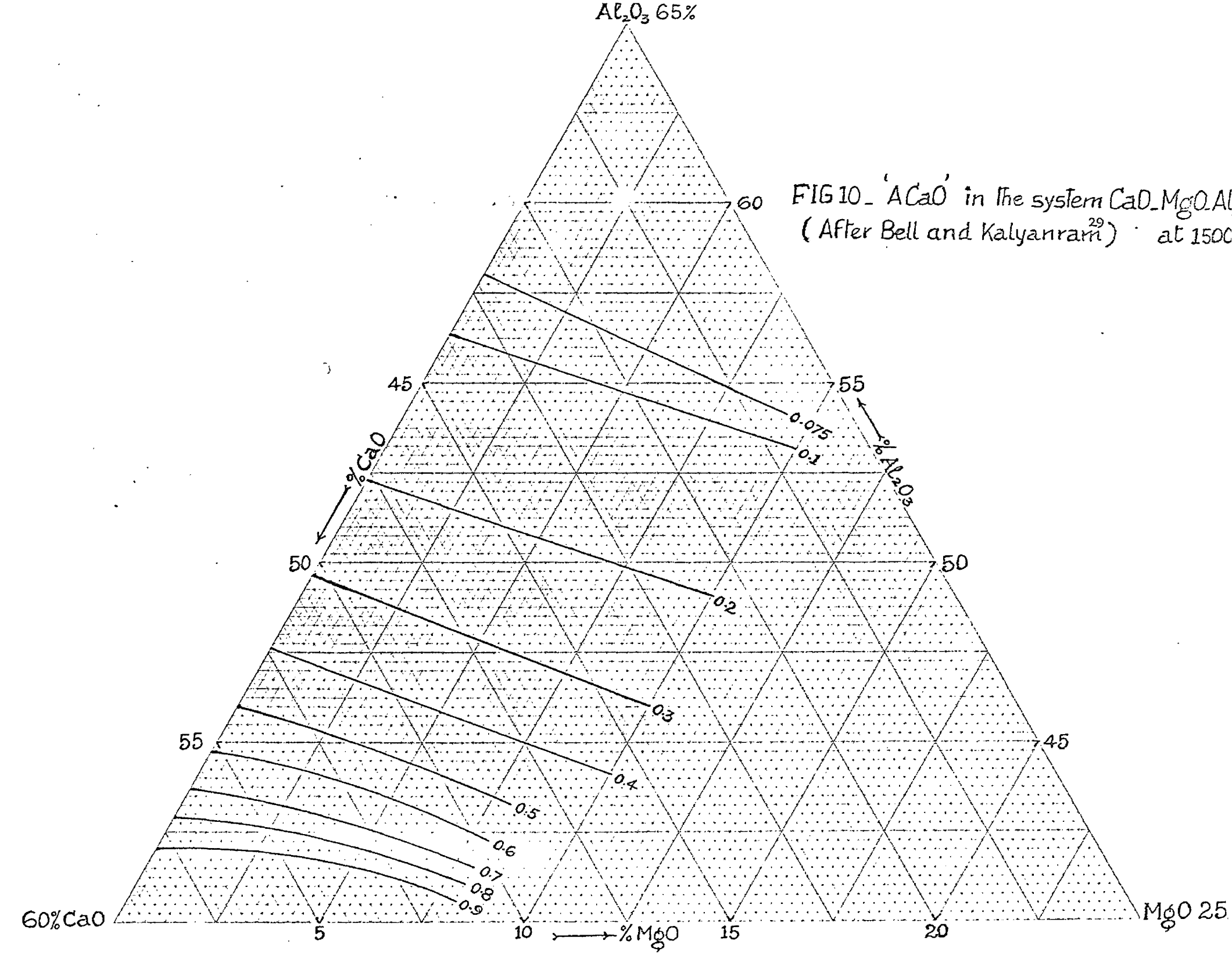


FIG 10 - 'ACaO' in the system CaO-MgO-Al
(After Bell and Kalyanram[29]) at 1500

From the data of Rosenqvist[20], the numerical value for the equilibrium constant at 1600°C and 1550°C are:-

$$K_{10}^{1600} = 2{\cdot}75 \times 10^{-2}$$

and $$K_{10}^{1550} = 3{\cdot}32 \times 10^{-2}$$

$$\therefore \quad \frac{K_{10}^{1550}}{K_{10}^{1600}} = 1{\cdot}2$$

i.e. $$\frac{C_S^{1550}}{C_S^{1600}} \times \frac{a_{CaO}^{1600}}{a_{CaO}^{1550}} = 1{\cdot}2,$$ assuming negligible temperature effect on γ_{CaS}.

Transposing the terms, this leads to the result,

$$C_S^{1550} = 1{\cdot}2 \times C_S^{1600} \times \frac{a_{CaO}^{1550}}{a_{CaO}^{1600}}$$

Chipman[33], while re-examining the results of Carter and Macfarlane[10] for lime-alumina slags in the light of compounds formed between lime and alumina, has concluded that the effect of temperature on the activity of lime from 1500 - 1550°C would be negligible. A similar conclusion has been reached by Sharma and Richardson[36] who investigated lime activities in the lime-silica system at 1500°C and 1550°C. It follows therefore that the temperature correction for sulphide capacity for both these systems from 1500-1550°C is 1·2.

That is,

$$C_S^{1660} = 1{\cdot}2 \times C_S^{1500}$$

$$= 1{\cdot}2 \times \frac{2}{307} \times A_{CaO}^{1500}$$

$$= \frac{2{\cdot}4}{307} \times A_{CaO}^{1500}.$$

This value agrees reasonably well with the limited data on the effect of temperature on the sulphide capacity of slags[16,19,35,60,80].

Sulphide capacities of lime-alumina-magnesia slags calculated in this way at 1500°C are given in Table 8. The sulphide capacities of lime-silica-magnesia slags used in this work cannot be directly computed using the ternary diagram lime-magnesia-silica (of Bell and Kalyanram[80]), because the slag compositions investigated here fall in the dicalcium silicate field where no direct activity data is available. Their diagram is reproduced in Fig. 11. However, the A_{CaO} in this region can be determined by an extrapolation method. This method consists in replotting their data in terms of A_{CaO} v. composition at constant magnesia (in this case 7·5% was used) and extrapolating the curve over a short interval to the point representing saturation with dicalcium silicate at 1500°C. $A_{CaO} = 0{\cdot}048$ was thus obtained. Since slags in the present study consist of liquid in equilibrium with dicalcium silicate at 1550°C, the A_{CaO} and hence the sulphide capacity of slags can be regarded substantially as constant. It can be seen that the sulphide capacity value so obtained ($C_S = 0{\cdot}375 \times 10^{-3}$) for lime-magnesia-silica slags, given in Table 9, is considerably lower than those for lime-alumina-magnesia slags shown in Table 8. These show the greater effect of silica compared with

TABLE 6. Calculated sulphide capacity and iron oxide activity, against mole fraction of ferrous oxide and calculated ionic fraction product of ferrous and oxide ion for lime-alumina-magnesia slags in equilibrium with molten iron at 1550°C.

Melt No.	$(\%S)/[a_s]$	$A^{1500\,°C}_{CaO}$	$C_S^{1550\,°C}$ x 10^5	a_{FeO} x 10^2	N_{FeO} x 10^2	$N_{Fe^{2+}} N_{O^{2-}}$ x 10^4
21	27·2	0·75	5·67	9·598	7·12	6·1
22	6	0·19	1·464	10·098	6·6	4·94
23	14·01	0·344	2·69	8·005	6·2	5·33
24	2·49	0·18	1·408	25·13	11·38	6·16
25	12·97	0·15	1·172	4·016	3·29	2·042
26	12·28	0·28	2·092	7·175	5·04	3·665
27	29·65	0·55	4·3	6·447	3·475	2·58
28	20	0·34	2·650	5·906	5·28	4·02
42	3·16	0·1042	1·52	22·2	13·26	11·6
44	6·35	0·3607	2·665	10·34	9·47	5·37
45	7·52	0·1883	1·472	8·69	8·03	5·57
46	33·4	0·4714	3·682	4·9	7·79	6·35
47	7·02	0·2583	2·02	12·76	10·98	8·45
48	10·83	0·37	3·60	15·92	9·10	9·12
50	3·78	0·175	1·368	25·65	32·3	25·3
51	3·56	0·3437	2·682	33·45	30·3	27·5
52	9·4	0·4857	3·8	31·2	30	22·7

TABLE 6 (Cont'd)

Melt No.	$(\%S)/[a_S]$	$A_{CaO}^{1500\,^{\circ}C}$	$C_S^{1550\,^{\circ}C} \times 10^3$	$a_{FeO} \times 10^3$	$N_{FeO} \times 10^3$	$N_{Fe^{+2}}$ $N_{O^{-2}} \times 10$
53	2·73	0·175	1·368	25·65	22·05	16·55
54	3·34	0·3125	2·445	32·5	28·6	20·3
55	5·6	0·5	3·915	31	35	31·4
56	2·7	0·25	1·955	32·15	42·2	31·4
57	3·27	0·3437	2·69	30·5	55·2	48·75
58	4·65	0·1562	1·22	11·64	10	7
59	4·44	0·38	2·61	28·1	31·6	26·5
60	6·12	0·1876	1·466	10·65	9·37	6·77
61	5·10	0·475	3·715	20·2	20·35	16·6
62	3·66	0·1696	1·330	19·25	11·65	9·04

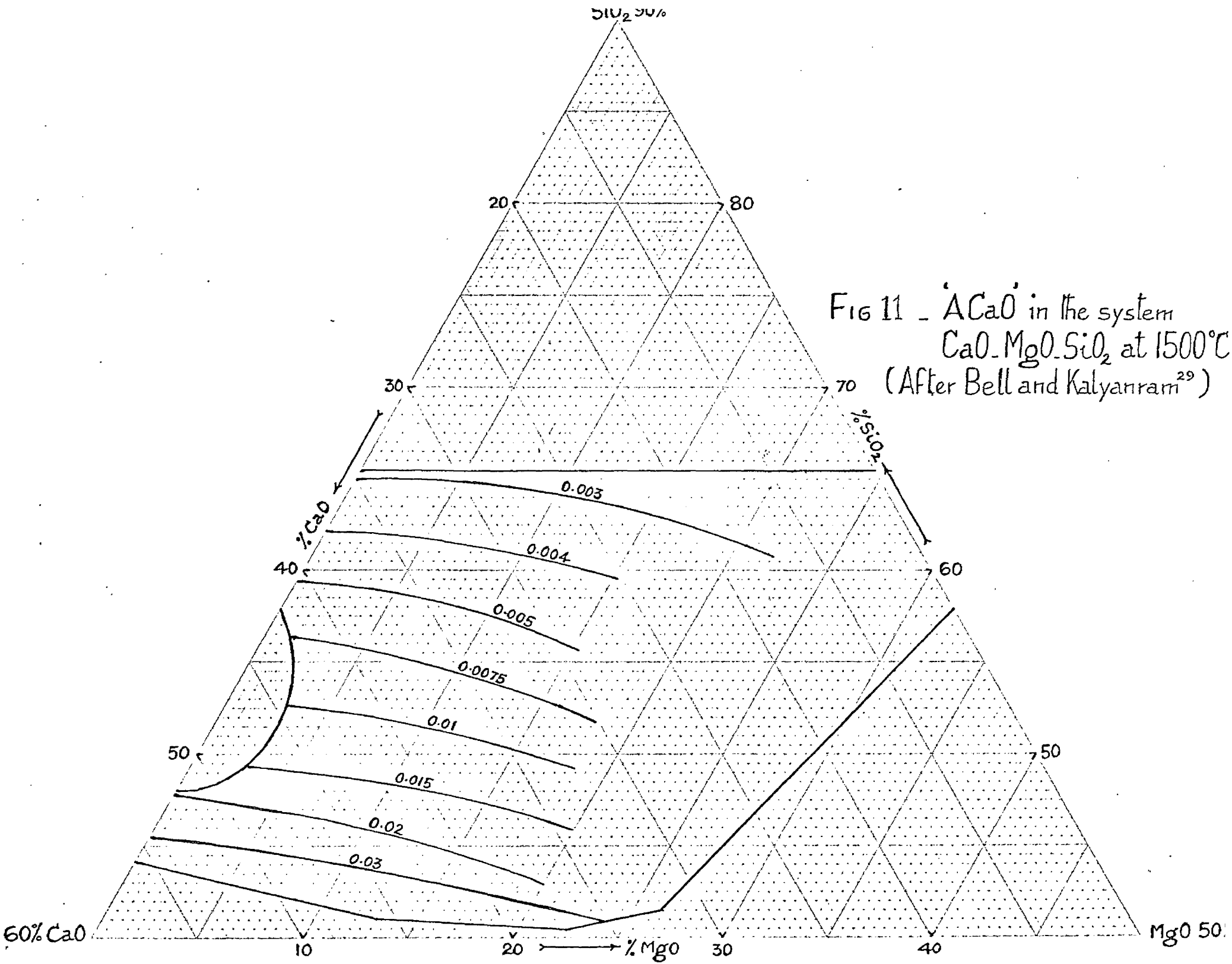


FIG 11 _ 'ACaO' in the system $CaO-MgO-SiO_2$ at 1500°C (After Bell and Kalyanram[29])

TABLE 9 Calculated sulphide capacity and iron oxide activity against mole fraction of ferrous oxide for lime-silica-magnesia slags in equilibrium with molten iron at 1550°C.

Melt No	(%S) / $[a_S]$	$A_{CaO}^{1500\,°C}$	$C_S^{1550\,°C} \times 10^3$	$a_{FeO} \times 10^0$	$N_{FeO} \times 10^3$
29A	2·73			6·06	6·67
$29D_4$	7·35			2·25	5·12
$29D_3$	5·2	0·026	0·375	3·16	5·12
30	12·19			1·28	7·63
31A	3·05			4·19	10·51
31B	1·66			9·65	10·16

TABLE 10 - Calculated sulphide capacity and iron oxide activity against mole fraction of ferrous oxide and calculated ionic fraction product of ferrous and oxide ion for lime-alumina-silica-magnesia slags in equilibrium with liquid iron at 1550°C.

Melt No.	(%S) / $[a_S]$	$A_{CaO}^{1500\,°C}$	$C_S^{1550\,°C} \times 10^3$	$a_{FeO} \times 10^3$	$N_{FeO} \times 10^3$	$N_{Fe^{+2}} \cdot N_{O^{-2}} \times 10^3$
34	14·25	0·2107	1·693	5·275	7·68	4·9
35	10·6	0·14	1·093	4·56	6·69	3·735
36	6·88	0·1295	0·965	6·225	6·45	3·575
37	16·68	0·4	3·125	8·325	9·65	6·32
38	12·64	0·19	1·464	5·145	5·65	3·625
39	7·5	0·13	1·026	6·02	8·63	4·6

alumina in reducing sulphide capacity.

In the case of lime-alumina-silica-magnesia slags, the sulphide capacities were derived using the same ternary diagram lime-magnesia-alumina. This involves the tacit assumption that silica in the range 4 - 5% has the same effect in lowering lime activity as the same amount of alumina. This implication can be examined in the light of the ternary diagram lime-alumina-silica of Carter and Macfarlane[10] showing the iso lime activity lines. This diagram is reproduced in Fig. 12. It can be seen that the iso lime activity lines run roughly parallel to the side opposite to the lime corner up to about 5% silica. This indicates that the replacement of alumina by 5% silica does not affect very much the lime activity. The sulphide capacities for lime alumina-silica-magnesia slags are given in Table 1v.

It is now possible to compute the activity of ferrous oxide in the slag combining sulphide capacity data and the distribution ratio with the appropriate thermodynamic data. This can be done as follows.

Considering the two equations,

$$[S]_{wt\%} = \tfrac{1}{2}S_2(g) \qquad \text{.....(2b)}$$

$$K_{(2b)} = \frac{P_{S_2}^{1/2}}{[a_S]}$$

and $$[Fe] + \tfrac{1}{2}O_2(g) = (FeO) \qquad \text{.....(25)}$$

$$K_{(25)} = \frac{(a_{FeO})}{P_{O_2}^{1/2}}$$

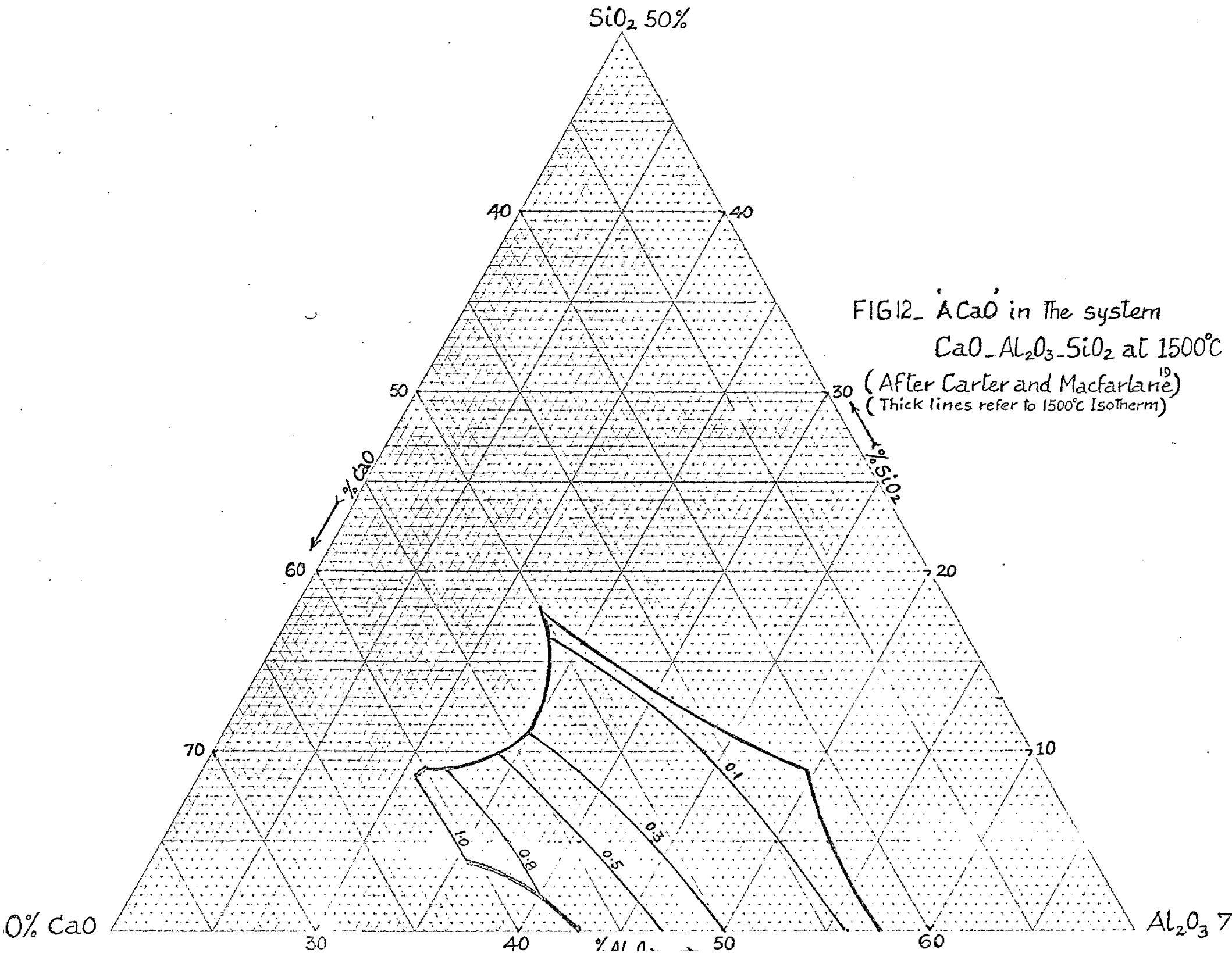


FIG12_ 'ACaO' in the system $CaO\_Al_2O_3\_SiO_2$ at 1500°C

(After Carter and Macfarlane[19])

(Thick lines refer to 1500°C Isotherm)

It follows that

$$K_{(2b)}\,K_{(s)} = \frac{p_{S_2}^{\frac{1}{2}}}{[a_S]} \times \frac{(a_{FeO})}{p_{O_2}^{\frac{1}{2}}}$$

Hence,

$$(a_{FeO}) = K_{(2b)}\,K_{(2S)}\,a_S \cdot \frac{[a_S]}{[\%S]}, \text{ since } a_S = (\%S)\,\frac{p_{O_2}^{\frac{1}{2}}}{p_{S_2}^{\frac{1}{2}}}$$

$$= K_{(2b)}K_{(ss)}\,\frac{a_S}{(\%S)}\,.$$

From the data of Sherman, Elvander and Chipman[6]

$$\Delta G^\circ_{(2b)} = -4{\cdot}575 \times T \times \log K_{(2b)} = +31{,}520 - 5{\cdot}27 \times T$$

$$\therefore K_{(2b)} = 2{\cdot}35 \times 10^{-3} \text{ at } 1550^\circ C.$$

From the data of Richardson et al, as compiled by Ward[46],

$$\Delta G^\circ_{(ss)} = -4{\cdot}575 \times T \times \log K_{(ss)} = -59{,}050 + 12{\cdot}855 \times T$$

$$\therefore K_{(2S)} = 10710 \text{ at } 1550^\circ C$$

Hence $(a_{FeO}) = 2{\cdot}35 \times 10^{-3} \times 10710 \times \frac{a_S}{(\%S)}$

$$= 44{\cdot}15 \times \frac{a_S}{(\%S)}$$

Since 'ferrous oxide' is non-stoichiometric, the activity so derived is relative to the cation deficient non stoichiometric oxide (wustite) as the standard state.

The iron oxide activities so derived from the sulphide capacity

of the slag and the distribution coefficient are given in tables 8 and 10. It can be seen from these tables that the activity values are nearly the same as the mole fraction of iron oxide calculated from slag analysis for lime-alumina and lime-alumina-silica slags. This can be regarded only as a fortuitous occurrence, as at low concentrations of any constituent in the slag Henrian behaviour is more likely than Raoultian behaviour. The computed iron oxide activity values for lime-silica slags show some variation of γ_{FeO} with composition (Table 9).

Ideal behaviour is not exhibited by the "ferrous oxide" in the liquid slag, especially basic slags. The work of Korber[88] and of Taylor and Chipman[90] indicate that in acid slags, the activity of ferrous oxide is approximately equal to the mole fraction. Later work of Schuhmann and Ensio[84], Fischer and Von Ende[88], and Bell[70] have shown that in acid slags, γ_{FeO} has values of 0·63, 0·9 and 0·85 respectively. In basic slags, the problem becomes more complex in view of the lack of knowledge of the correct constitution of liquid slag. In order to explain the deviation from ideality in basic slags (Fig. 13) Fetters and Chipman[88] in their study of the distribution of oxygen between carbon-free iron and slags of the system $CaO-FeO-Fe_2O_3$, assumed the formation of the compound $CaO-Fe_2O_3$. The mole fraction of ferrous oxide was then calculated adjusting for the formation of

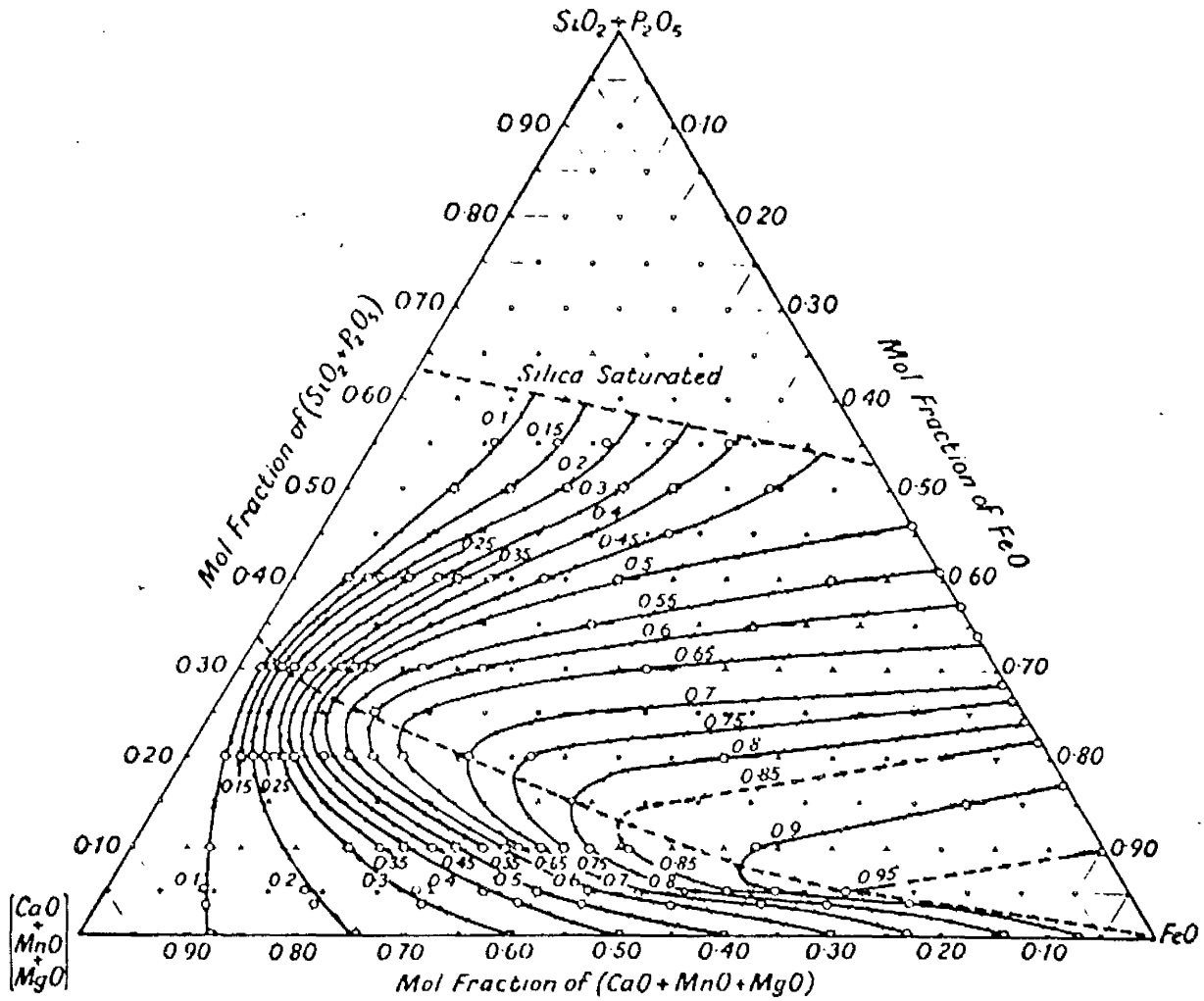


FIG. 13. Variation of the activity of iron oxide with composition in simple synthetic laboratory slags at steel-making temperatures (from Turkdogan and Pearson [90]).

$CaO.Fe_2O_3$ and little $2CaO.SiO_2$ (for the presence of small amounts of silica in their slags). Closer agreement to Raoult's law has been found by such a method. The modern trend, however, is to relate the activity of any slag constituent with the activities of its ions[60]. This would necessitate the correct knowledge of the liquid slag constitution, i.e. the ionic species present at any slag constitution.

In Fig. 16, the ferrous oxide activity has been plotted against the mole fraction. It can be seen that the points in the figure show little scatter about the Raoultian line. The points corresponding to the melts 56 and 57 are of interest. These slags contained higher percentages of iron oxide. As seen earlier, these were first subjected to total iron oxide analysis and subsequently to true ferrous oxide analysis. The mole fractions calculated in both cases, showed that the agreement to Raoult's law is better in the case of the latter. . In the figure the points 56 and 57 refer to the mole fractions calculated on the basis of true ferrous oxide. The discrepancy shown by point 57 can only be attributed to the non-attainment of equilibrium or some other experimental error.

It may be seen from the plot that at very low concentrations, most of the points for lime-alumina slags are above the Raoultian line and those for lime-alumina-silica slags are below it showing a tendency for immiscibility in the case of iron oxide and alumina and a tendency for compound formation between iron oxide and silica.

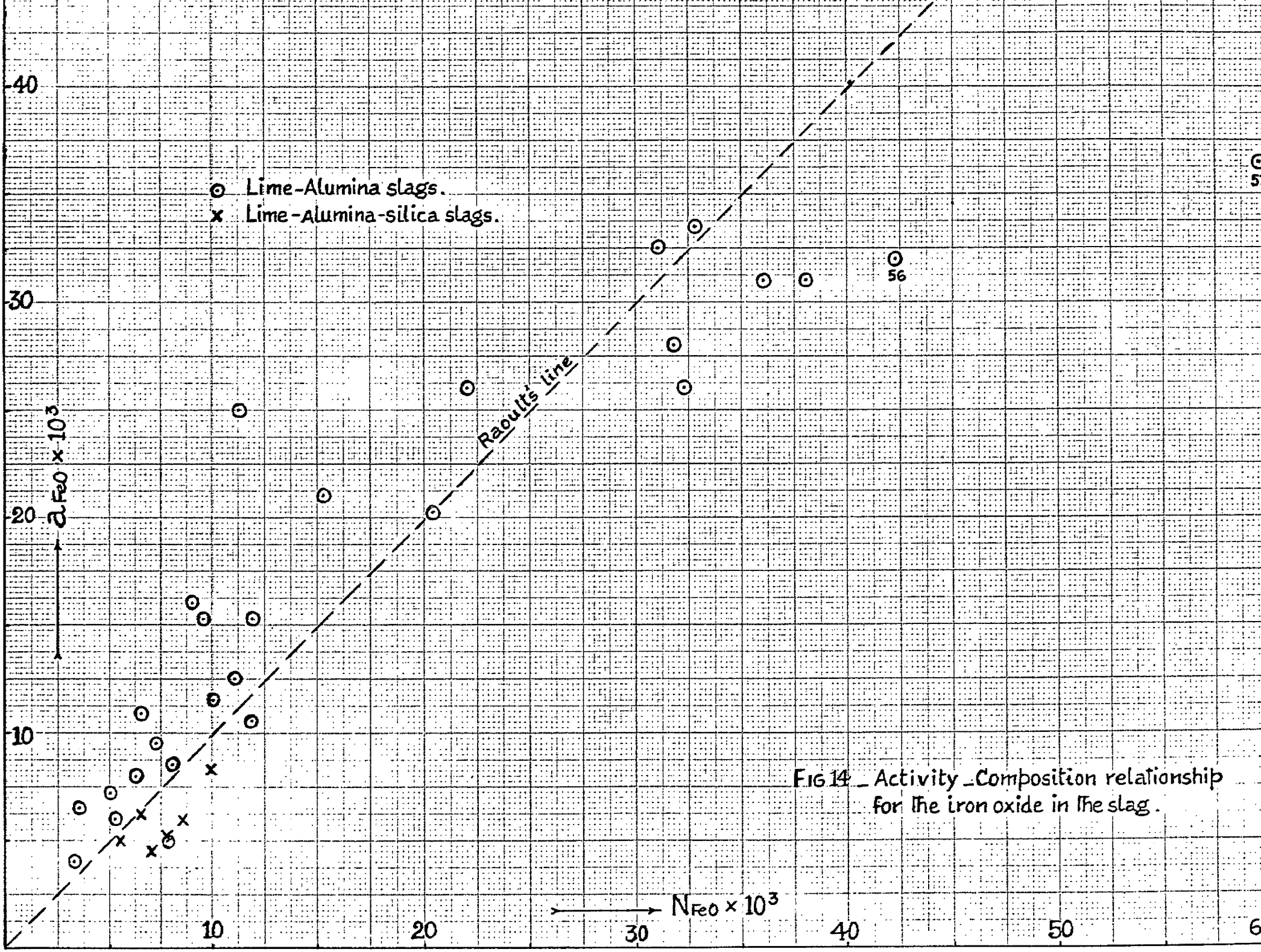


FIG 14 _ Activity _ Composition relationship for the iron oxide in the slag.

but this cannot be fully justified and it appears that the scatter about the ideal line can only be attributed to experimental errors in slag-metal and gas-slag work and the accuracies in the thermodynamic data used in computing iron oxide activity.

It will be interesting to study the variation of activity of iron oxide with composition for different slags. One diagram from Turkdogan and Pearson[66] showing the iso iron oxide activity lines in slag system composed of simple synthetic slags at steel making temperatures is reproduced in Fig. 13. It can be seen from the figure that within the concentration range 0·65 to 0·75 mole fraction of CaO + MnO + MgO, the iso activity curve for $a_{FeO} = 0.1$ does not show marked deviation from ideality. So at lower concentration range of ferrous oxide, ideal behaviour is more likely in this concentration range. This conclusion can be arrived at from an examination of the trend of iso ferrous oxide activity lines. Substitution of alumina for silica may not show any marked change in the course of iso activity curve especially in the above range of concentration. It may also be noted that for the slags used in this work, the ferrous oxide activities are of the order of 10^{-3}.

The influence of ferrous oxide content of the slag on sulphur partition can also be visualised through a plot of $(\%S)(a_{FeO})/[a_S]$ v. excess base. Fig. 15 shows increase of this ratio with increase in basicity due to increase in both the terms $(\%S)/[a_S]$ and a_{FeO}.

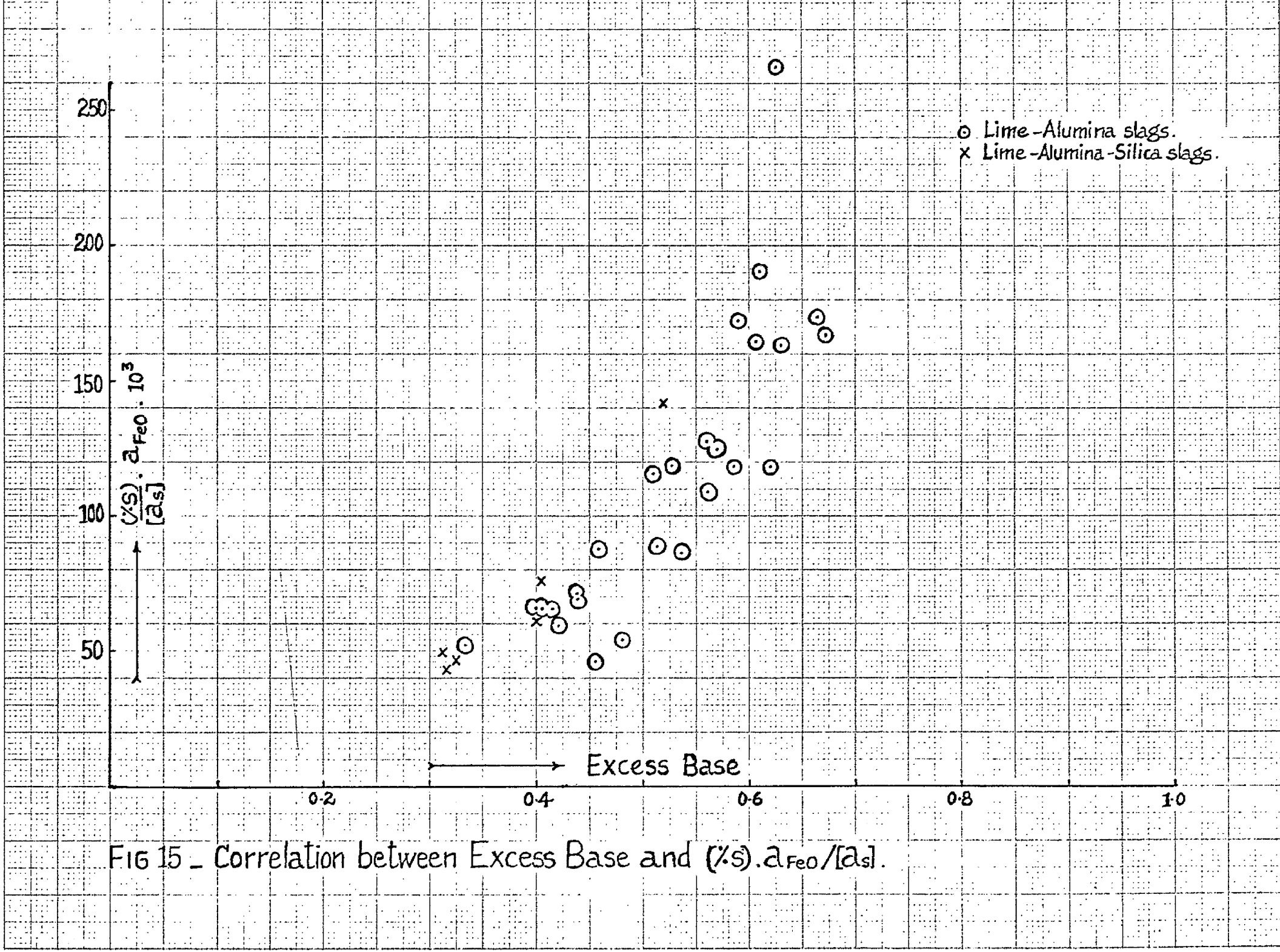


FIG 15 _ Correlation between Excess Base and $(\%S).a_{FeO}/[a_S]$.

The function $(\%S)(a_{FeO})/[a_S]$ is similar to the "S - O ratio" of Chipman et al[63,64], i.e. $(\%S).[\%O]/[a_S]$. Fig. 15 also resembles the plot of distribution coefficient v. excess base of Intch and Chipman[en] where the oxygen potential has been regarded as constant. It can be seen that the points show wide scatter. The points for lime-alumina-silica slags do not correlate well with those for lime-alumina slags and can be represented by a separate curve. This implies that in the expression,

$$CaO + \tfrac{2}{3} MgO + (SiO_2 + Al_2O_3)$$

silica and alumina are not exactly equivalent in reducing basicity on a mol basis. It seems to suggest that on a mol basis silica is more effective in reducing basicity for a satisfactory correlation Furthermore, the scatter is in part explicable by the assumption that magnesia is equivalent to 2/3 lime on a mol basis. It may be pointed out that the 'excess base' expression has been developed by Intch and Chipman for higher silica contents (30-43%) and lower alumina contents (10-26%) than are encountered in slags used in this investigation.

Taylor and Stobo[66] have re-examined the ability of the function 'excess base' to correlate with oxide ion activity, while plotting their $(\%S)/[a_S]$ ratio v 'excess base' along with the data of Intch and Chipman. It was found that in low alumina slags (ca 10%) the function is overestimated and for high alumina slags (ca 20%) it is underestimated. This indicates that as the alumina content

of the slag increases, there is a tendency for its behaviour to become less acidic, in other words, it shows amphoteric properties. This has also been indicated by Kulikov et al[80].

The study of the variation of sulphur distribution with the sulphide capacity of the slag for various iron oxide contents will be of interest. The implication of such a plot is that both the functions $(\%S)[a_O]/[a_S]$ and C_S are directly proportional to the function $(a_{O^{--}})/(\nu_{S^{--}})$. Hence the plot should be straight lines passing through the origin for various iron oxide contents. In Fig. 16A, this plot has been made and straight lines have been drawn for approximate iron oxide contents through the origin. It will be seen that for constant sulphide capacity of the slag, ie. at constant oxide ion activity (neglecting any variation in $\nu_{O^{--}}$) iron oxide in low concentrations has relatively greater effect in reducing the distribution ratio than at higher concentrations. This trend has already been observed in Fig. 9 showing the effect of iron oxide on the distribution ratio for various basicities.

No data are available for comparison in the region of iron oxide contents encountered here. It is possible, however, to calculate $[f_S]$ and hence $(\%S)/[\%S]$ figures from the results of Hatch and Chipman[80] at 1500°C by the application of Chuiman-Chipman[10] - Morris-Buehl[7] method to account for the effect of carbon, silicon and the small amounts of sulphur in molten iron on the activity coefficient of sulphur. The

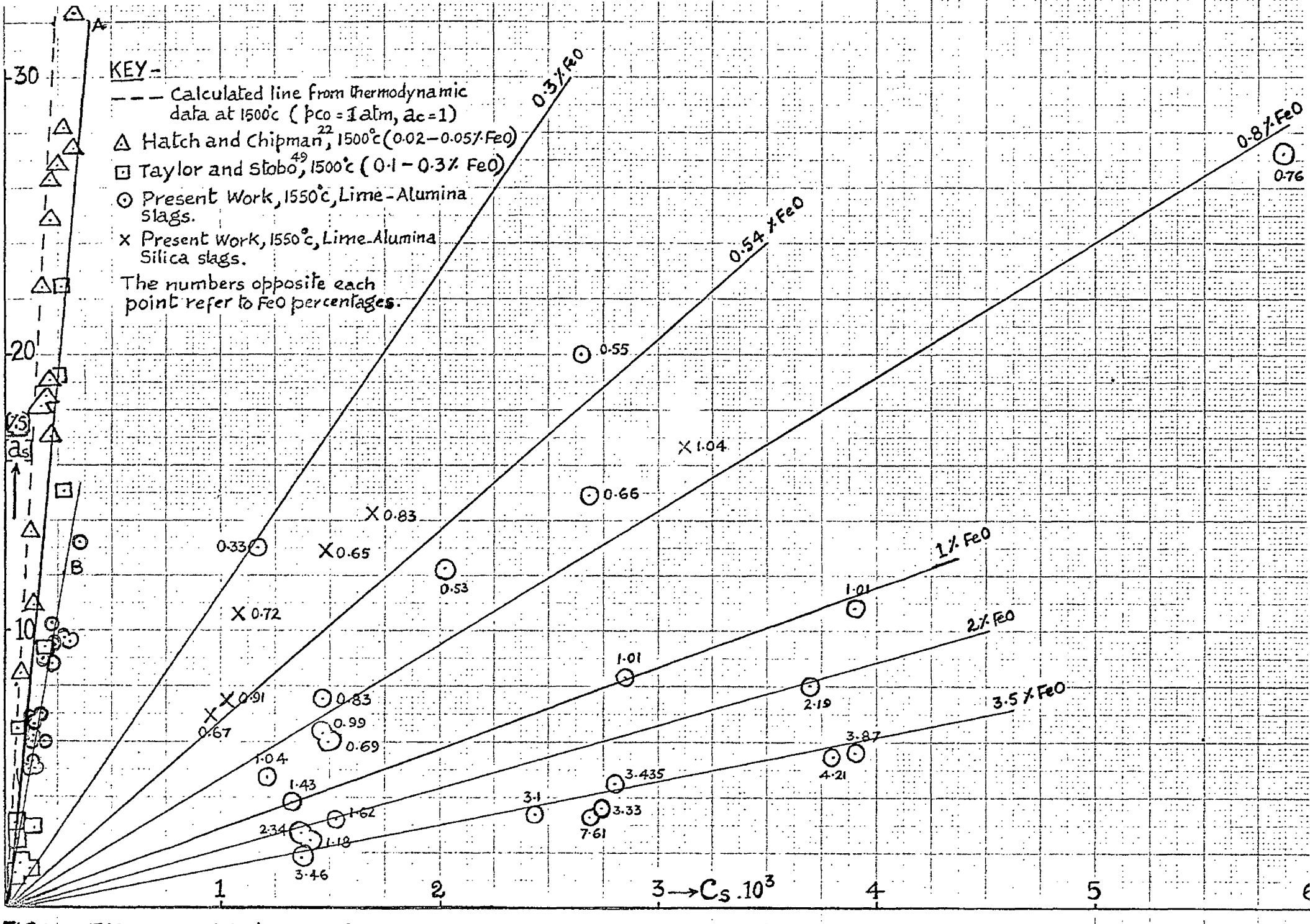


FIG16A_Effect of sulphide capacity and oxygen potential on sulphur distribution between slag and metal.

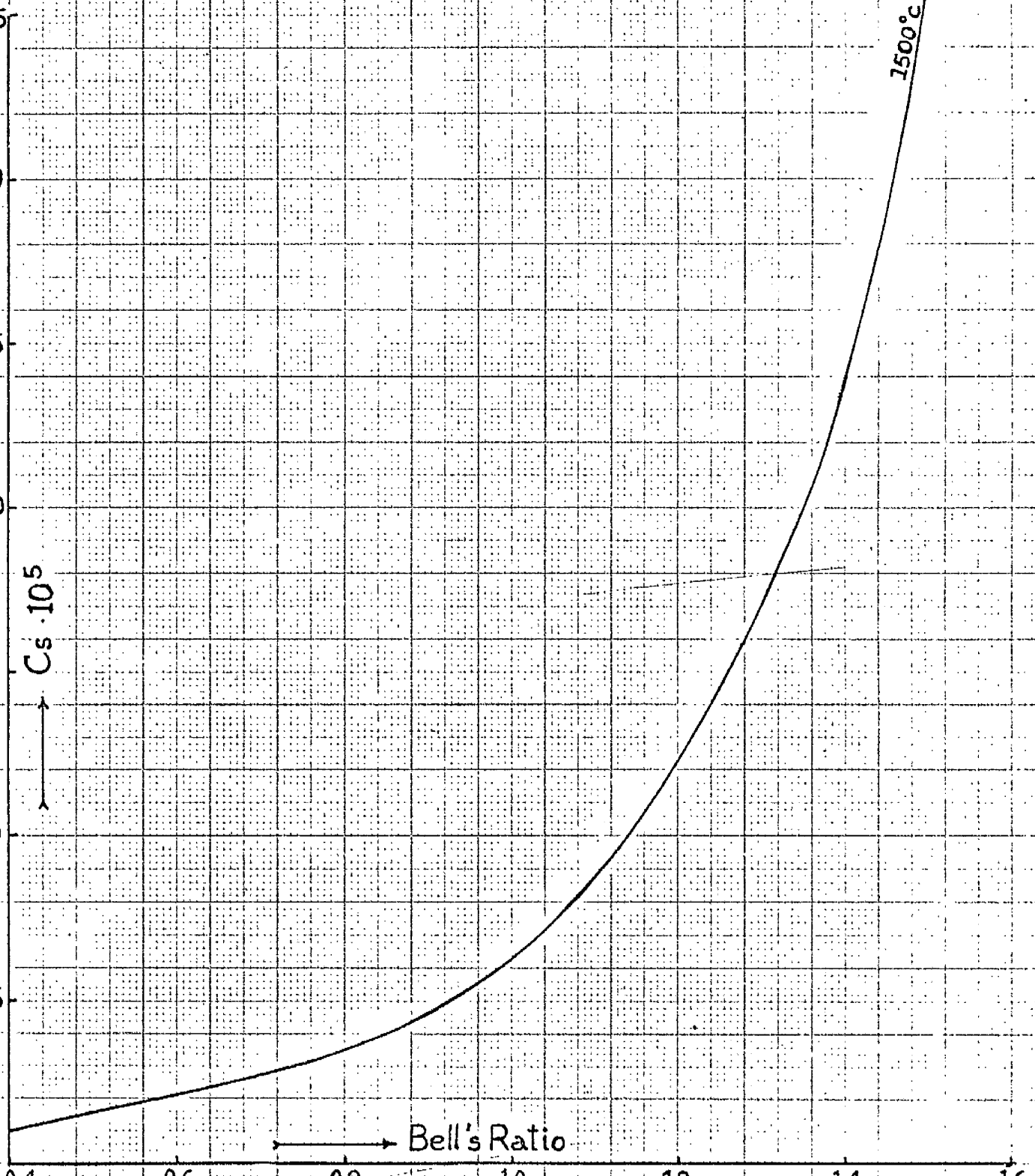


FIG16B Sulphide Capacities of $CaO-Al_2O_3-MgO-SiO_2$ slags. (after Kalyanram et al[25])

sulphide capacities for their slags are calculable from Fig. 16b, after Kalyonnen et al[86], representing the variation of sulphide capacity with Boll's ratio for lime-alumina-magnesia-silica slags at 1500°C. The results of Taylor and Stobo[60] are also plotted in the same way (FIG 16A) and they agree reasonably well with Natch and Chipman. The experiments of Taylor and Stobo in carbon crucibles contained greater amounts of iron oxide (0·1 - 0·3%) than those of Natch and Chipman (0·02 - 0·05%) and this explains the lesser slope of the line joining the points of Taylor and Stobo compared with that of Natch and Chipman. The results of Taylor and Stobo in alumina crucible experiments and those of Kulikov et al[87] are difficult to plot here in view of the very low distribution ration of the former and high distribution ratios of the latter. The line calculated from thermodynamic data at 1500°C using p_{CO} = 1 atmosphere and a_C = 1 is also shown in the figure as dotted line. By thermodynamic calculations, it can be shown that

$$C_S \times 10^0 = \frac{(\%S)}{[\%S]} = 0{\cdot}7302$$

i.e. the slope of the dotted line in the figure is 137.

All these data at 1500°C correlate well with the present results at 1550°C in that the various straight lines form a fan-like pattern from the origin.

In Fig. 17, the distribution ratio $(\%S)/[\%S]$ has been plotted against the activity of iron oxide for different basicity values. These curves show similar trend as those in Fig. 9.

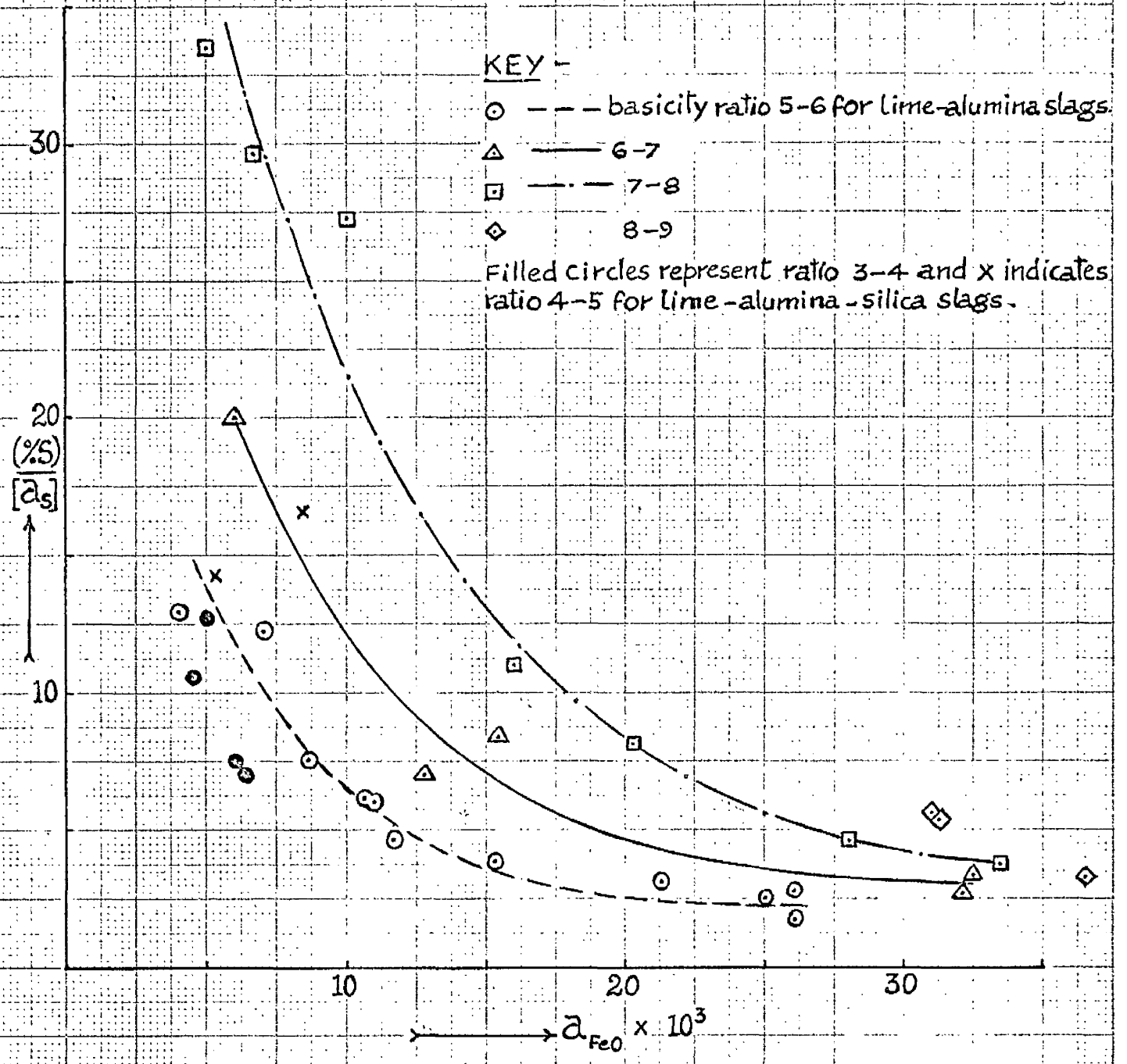


FIG 17 - Effect of basicity (Bell's Ratio) and of iron oxide activity in the slag on the equilibrium distribution coefficient of sulphur at 1550°C.

(C) Effect of basicity on the solubility of Calcium Sulphide in Slags.

Little information exists on the effect of basicity on the solubility of calcium sulphide in slags and there is some controversy about this behaviour. The solubility of calcium sulphide under different slag compositions reported by various workers has been given previously in Table 3, page 54 . So even if approximate values of the solubilities are available, they might be of some value. It was generally considered that the solubility of calcium sulphide increases with basicity, i.e. with increase in lime content. Hence a decrease in the activity coefficient of calcium sulphide with basicity is to be expected. Recent investigations have shown that this need not necessarily be so.

Bell et al[88], while reexamining the results of Hatch and Chipman[22], have shown that the plot of $(\%S)/[a_O]$ v. A_{CaO} can be represented better by a curve of increasing slope. The oxygen potential in the experiments of Hatch and Chipman being regarded as constant, it follows that both $(\%S)/[a_O]$ and A_{CaO} are direct functions of $(a_{O^{--}})/(\gamma_{O^{--}})$. A curved plot therefore implies that $(\gamma_{O^{--}})$ is not constant and it decreases with increasing basicity. In other words, the solubility of calcium sulphide increases with increasing basicity. This agrees with the work of Sharma and Richardson who found increases in solubility of calcium sulphide with increase in CaO/Al_2O_3 ratio in lime-alumina melts[81]; but the opposite effect was found by the same workers in lime-silica melts.[84]

McCaffery and Custerla[91], however, reported that the effect of alumina is to increase the solubility of calcium sulphide in lime-alumina-silica slags. According to them the actual chemical composition of the slag is of less importance than the temperature in affecting sulphur solubility. The results of Taylor and Gibbons[88] also indicate increase in sulphur solubility in CaO-Al_2O_3 slags with increase in alumina content. From the results of the present investigation, however, it is possible to assess approximately the solubility of calcium sulphide in lime-alumina and lime-alumina-silica slags and to study the trend with composition with certain approximations. This could be done by a consideration of metal-gas, slag-gas and slag-metal equilibria, as follows.

$$[S]_{wt\ \%} = \tfrac{1}{2} S_2(g) \qquad \ldots\ldots\ldots\ldots (2b)$$

$$\text{and } K_{(2b)} = \frac{P_{S_2}^{1/2}}{[a_S]}$$

$$[O]_{wt\ \%} = \tfrac{1}{2} O_2(g) \qquad \ldots\ldots\ldots\ldots (2c)$$

$$\text{and } K_{2c} = \frac{P_{O_2}^{1/2}}{[a_O]}$$

$$(O^{--}) + \tfrac{1}{2} S_2(g) = (S^{--}) + \tfrac{1}{2} O_2(g) \ldots\ldots\ldots (11)$$

$$\text{and } K_{(11)} = \frac{(a_{S^{--}})\, P_{O_2}^{1/2}}{(a_{O^{--}})\, P_{S_2}^{1/2}}$$

$$(O^{-2}) + \underline{S} = (S^{-2}) + \underline{O} \qquad \ldots\ldots\ldots\ldots (15)$$

$$\text{and } K_{15} = \frac{(a_{S^{-2}})\,[a_O]}{(a_{O^{-2}})\,[a_S]}$$

It follows that,

$$K_{1.5} = \frac{K_{(2b)}K_{(11)}}{K_{(26)}}$$

$K_{(2b)}$ = $2 \cdot 36 \times 10^{-3}$ as calculated earlier.

From the results of Chipman et al, as given by Ward[55],

$$\Delta G_{(26)} = -3 \cdot 675 \times T \times \log K_{(26)} = 20230 + 0 \cdot 57 \times T$$

$$\therefore \quad K_{(26)} = 3 \cdot 097 \times 10^{-4} \text{ at } 1550°C.$$

From the data of Rosenqvist[20], $K_{(11)} = 3 \cdot 32 \times 10^{-3}$ at 1550°C.

Hence, $K_{(15)} = \frac{3 \cdot 32 \times 10^{-3} \times 2 \cdot 36 \times 10^{-3}}{3 \cdot 097 \times 10^{-4}}$

$= 0 \cdot 0253$

i.e. $$\frac{(a_S^{-2})[a_O]}{(a_O^{-2})[a_S]} = 0 \cdot 0253$$

Transposing the terms and assuming Henrian behaviour of oxygen in the metal, we obtain

$$(a_{S^{--}}) = \frac{0 \cdot 0253 \cdot (a_O^{-2})[a_S]}{[\%O]}$$

$$= \frac{0 \cdot 0253 \times (a_O^{-2})}{0 \cdot 19 \times \frac{(a_{FeO})}{[a_O]}} \text{ since } \frac{[\%O]}{a_{FeO}} = 0 \cdot 19 \text{ at } 1550°C.$$

$$= \frac{0 \cdot 1332 \times (a_O^{-2})}{\frac{(a_{FeO})}{[a_S]}}$$

The oxide ion activities have not been determined experimentally for a slag composed of lime, alumina, magnesia, iron oxide and silica. However, lime activity values are available for lime-alumina melts from the work of Taylor and Gibbons[88] extended by Taylor and Chipman[89]. Their diagram is reproduced in Fig. 18. To derive the oxide ion activity of slags used in the present work, a certain approximation is necessary, namely, that magnesia and the small amounts of iron oxide encountered in these slags do not effect very much the sulphide capacity or the activity of lime in the slag. The validity of this assumption can be examined in the light of Kalyanram's plot[29] showing the effect of magnesia addition on the "lime equivalent" (i.e. oxide ion activity) for constant CaO/Al_2O_3 ratios. This diagram, converted to the sulphide capacity scale and corrected for the temperature effect, is reproduced in Fig. 19. It can be seen from this figure that the sulphide capacity shows a slight increase with increase in magnesia at constant C/A ratio and further that, within the limits of experimental error, it appears that this effect is greater at high C/A ratios. The C/A ratios encountered here are in the range 0·8 - 1·25. It may therefore be concluded that the approximation is more accurate at lower lime contents. $(a_{O^{--}})$ can therefore be obtained from Fig. 18, calculating lime per cent on a $CaO-MgO-FeO_x$ free basis. This calculation can be illustrated by melt 21 having the following slag analysis.

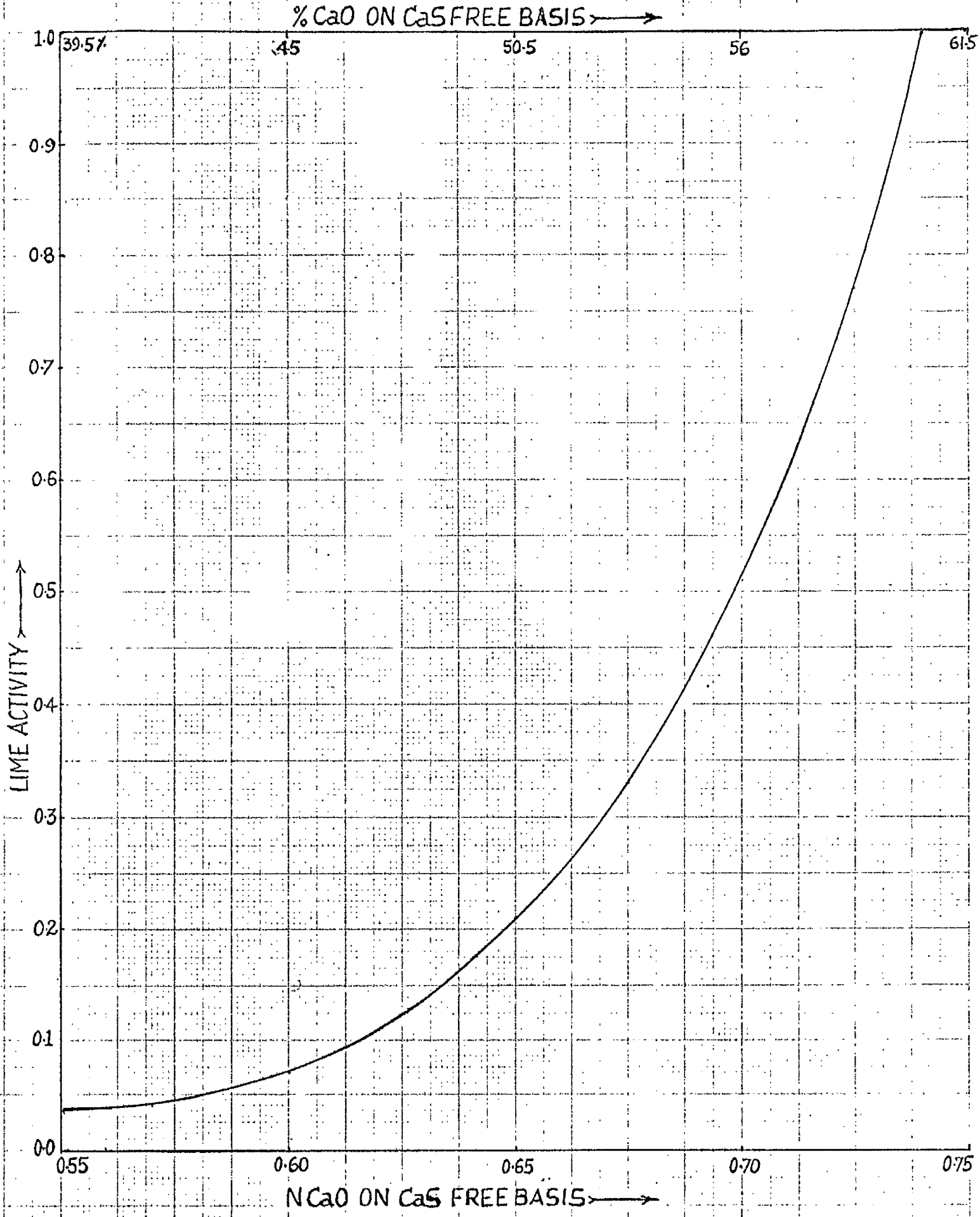


FIG 18 _ Lime activities in CaS-saturated Lime-Alumina melts at 1550°C
(After Taylor, Gibbons[32] and Cameron[33])

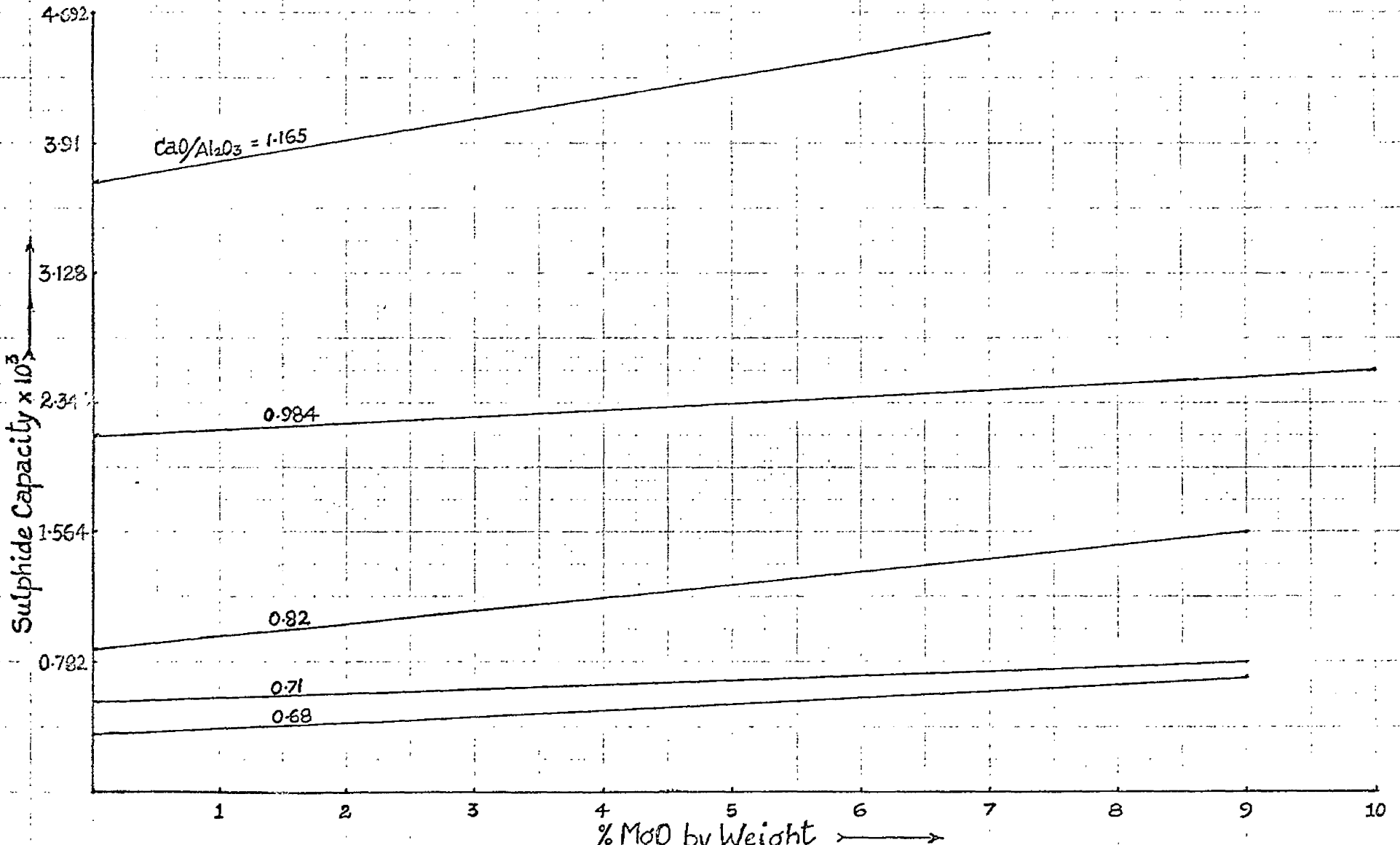


FIG 19 _ Effect of Magnesia on Sulphide Capacity for Slags of various Lime-Alumina ratios at 1550°c
(After Bell and Kalyanram[29])

$(CaO)_{true}$ = 50·18%

CaS = 1·93

MgO = 6·27

FeO = 0·76

Al_2O_3 = 40·87

Hence lime percent on a CaO-MgO-FeO_x free basis = $\frac{50.18}{91.06} \times 100$

= 55·1%

From Fig. 18, the activity of lime corresponding to this percentage = 0·45

From the present results

$$\frac{(a_{FeO})}{[a_S]} = \frac{9.598 \times 10^{-3}}{0.0328} = 292.2 \times 10^{-3}$$

Hence, $(a_{S^{-2}}) = \frac{0.1932 \times 0.45}{0.2902} = 0.2005$

These activity values are given in Table 11. As a second assumption it is can be considered that $\gamma_{S^{-2}}$ is nearly constant, then (%S) at saturation is given by the relation

$$(\%S)_{sat} = \frac{(\%S)}{(a_{S^{-2}})}$$

For slag 21, $(\%S)_{sat} = \frac{0.89}{0.2005} = 4.44$

These saturation sulphur solubilities are also given in Table 11.

For the lime-alumina-silica slags (melts 34 -39), the lime activity values are computed from the ternary diagram lime-alumina-silica after Gibbons and Taylor[66] and being extended by Cameron. This is reproduced in Fig. 20. The percent lime is calculated on a CaO-MgO-$(FeO)_x$ free basis as shown previously and $(\%S)_{sat}$ computed from it.

TABLE II - Saturation sulphur solubilities in lime-alumina-magnesia and lime-alumina-silica-magnesia slags against composition.

Melt No	% CaO (on free basis)	$a_{S^{--}}$	(%S)	$(\%S)_{Sat.}$
21	55·1	0·2005	0·89	6·44
22	44·5	0·081	0·868	8·25
23	49·8	0·1617	0·8065	4·99
24	45·5	0·0272	0·1595	5·87
25	43·15	0·1458	1·284	8·675
26	46·5	0·1048	1·285	6·6
27	52·7	0·666	3·29	4·78
28	49·5	0·271	1·416	5·22
34	46	0·1165	1·314	11·28
35	43	0·0098	1·2125	12·14
36	41·25	0·0585	1·107	18·9
37	50·4	0·442	2·505	5·66
38	48·7	0·144	1·764	12·4
39	40·5	0·0851	1·695	19·9
42	45·6	0·00755	0·4217	6·24
44	50·1	0·2242	1·08	4·81
45	44·75	0·185	1·2925	6·99
46	51·25	0·348	1·765	5·12
47	46	0·234	1·596	7·46
48	49·5	0·1532	1·125	7·2

TABLE II (cont'd)

Melt No	% CaO (on free basis)	σ_{sl}	(γ_s)	$(\gamma_s)_{sat.}$
50	44·8	0·18	0·668	4·93
51	50·4	0·2565	1·092	4·26
52	50·05	0·453	1·363	3·01
53	44·1	0·1302	1·15	8·5
54	49·5	0·3638	1·266	4·0
55	53·75	0·591	1·66	3·18
56	48·8	0·2058	0·8915	4·335
57	53·55	0·505	0·729	8·06
58	49	0·1152	1·044	9·06
59	51·25	0·2664	1·0435	3·91
60	43·8	0·1703	1·438	6·15
61	53·7	0·387	1·495	3·86
62	43·4	0·123	1·2665	8·63

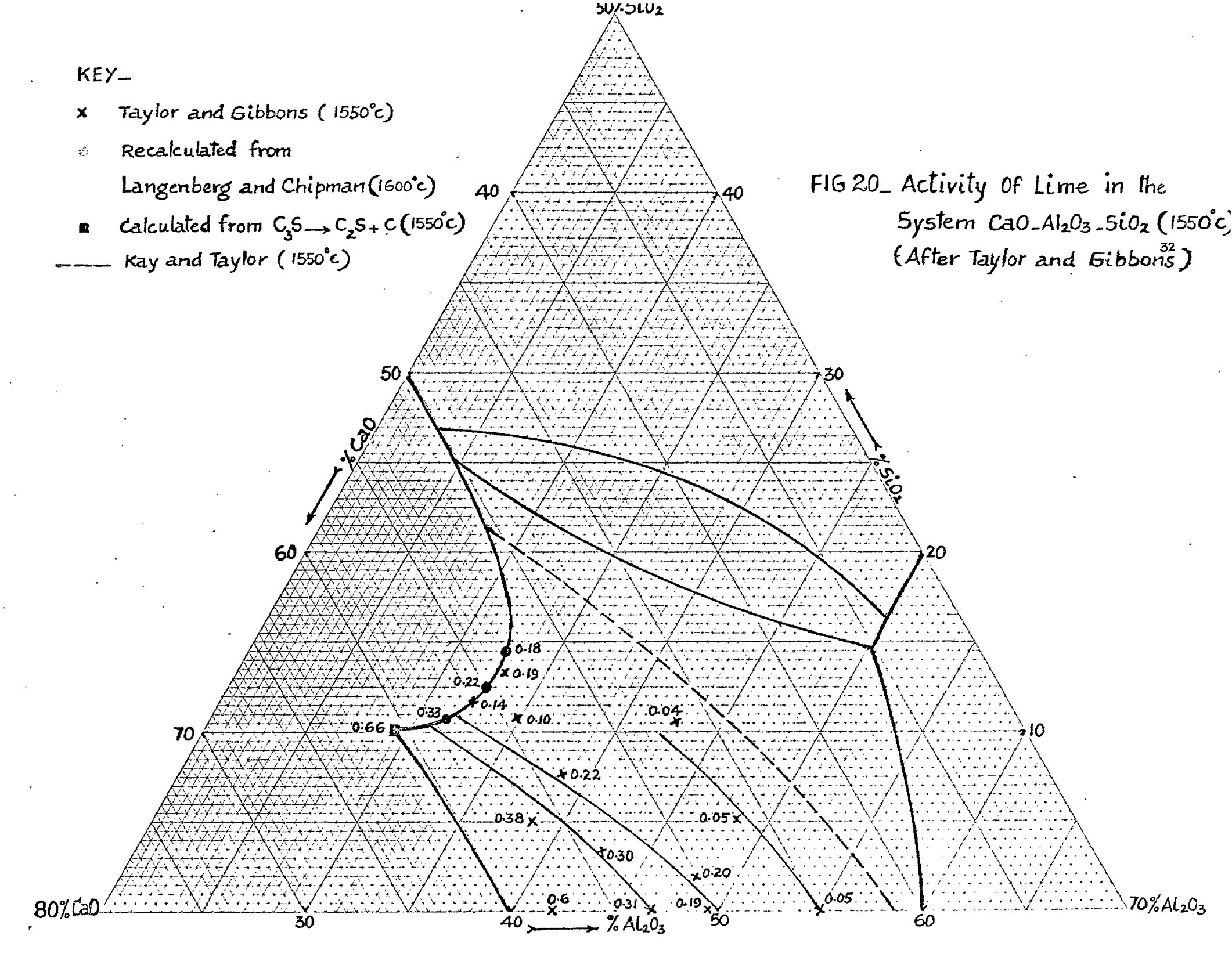


FIG 20– Activity of Lime in the System $CaO-Al_2O_3-SiO_2$ (1550°c) (After Taylor and Gibbons[32])

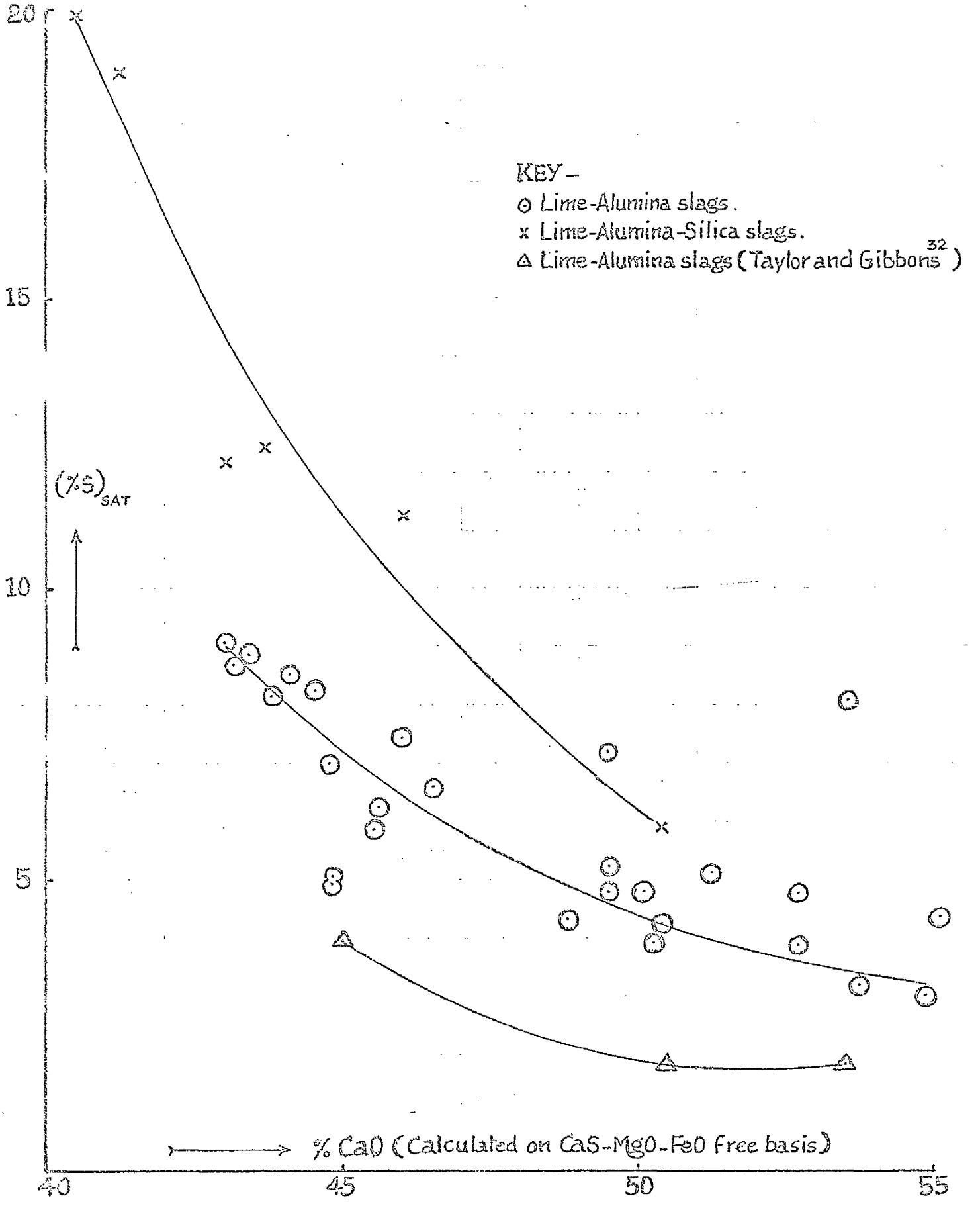


FIG 21 – Effect of composition on the solubility of sulphur in Lime-Alumina and Lime-Alumina-Silica slags.

In Fig. 21, $(\%S)_{sat}$ has been plotted against % lime calculated on a $CaO-MgO-FeO_t$ free basis. For comparison the solubility line of Gibbons and Taylor is also reproduced in the figure.

The calculated solubility curves are higher than the experimental solubility curve probably due to the assumptions made in the calculation. It can be seen that the lime-alumina-silica slags have much higher sulphur solubility especially at low lime contents. However, the same trend of decrease in sulphur solubility with increase in basicity is shown by all the three curves.

(2) APPLICATION OF TEMKIN'S THEORY

It has been seen during the course of literature survey that either the molecular theory of slag constitution or the more recent ionic theories can satisfactorily explain the slag-metal sulphur partition in terms of the equilibrium constants. The choice of the species under consideration, whether molecule or ion, is immaterial from a purely thermodynamic standpoint as the treatment is based on the activity concept. It depends more upon the particular conditions under investigation. The present knowledge of liquid slags, however, are more in favour of the latter concept and so it appears worth while to talk of the ionic species in slag such as Fe^{++} or $O^{=}$ etc. rather than molecules of FeO, etc. Treatment of liquid slags in this way suffers from the lack of knowledge of the dissociation of the constituent oxides in the liquid slag. The truth probably lies in between the two extremes, that slags are partially ionised as suggested by Kheiman[66].

Although, as seen earlier, the Herasymenko's model[69] of liquid slag assumed ideal or random mixing of the constituent ions irrespective of their sign or charge, Temkin[66] realised that this was impossible. He assumed ideal mixing of ions of the same charge and calculated the ionic fractions as

$$N_M^{+} = \frac{n_M^{+}}{\sum n_{cations}} \quad \text{and} \quad N_A^{-} = \frac{n_A^{-}}{\sum n_{anions}}$$

where n_M^{+} and n_A^{-} represent the number of M^{+} cations and A^{-} anions respectively. This concept is quite interesting in that it has established thought in terms of slag constitution, namely, the ionic species that are likely to be present at a given composition of slag.

When cations mix randomly with each other and anions also behave in the same way, the free energy of formation of any constituent, say ferrous oxide, is given by,

$$G_{FeO}^{M} = G_{Fe^{+2}}^{M} + G_{O^{-2}}^{M}$$

$$= RT \ln N_{Fe^{+2}} + RT \ln N_{O^{-2}}$$

$$= RT \ln N_{Fe^{+2}} N_{O^{-2}}$$

Identifying this with $RT \ln a_{FeO}$, we obtain

$$a_{FeO} = N_{Fe^{+2}} \times N_{O^{-2}}$$

i.e. the activity of any constituent is the product of the ionic fractions, the ions having the same sign and charge. The same conclusion can be reached by assuming complete dissociation of ferrous oxide, when

$$a_{FeO} = a_{Fe^{+2}} \cdot a_{O^{-2}}$$

$$= N_{Fe^{+2}} \gamma_{Fe^{+2}} \cdot N_{O^{-2}} \gamma_{O^{-2}}$$

$$= N_{Fe^{+2}} \cdot N_{O^{-2}} \quad \text{since} \quad \gamma_{Fe^{+2}} = \gamma_{O^{-2}} = 1.$$

'Ferrous oxide' is, however, non-stoichiometric. According to Elliot and Gleiser[88], the formula is $Fe_{0.947}O$ (for wustite in equilibrium with liquid iron). A small correction therefore appears necessary in the above equation. Darken and Gurry[100] have determined the ratio of ferric oxide to ferrous oxide by melting ferrous oxide in iron crucibles. According to their work (Ref. 70)

$$\frac{N_{Fe_2O_3}}{N_{FeO}} = 0.0525$$

Hence $$\frac{N_{Fe^{+3}}}{N_{Fe^{+2}}} = \frac{2 \times 0.0525}{0.947} = \frac{0.105}{0.947}$$

$$\therefore \quad N_{Fe^{+3}} = \frac{Fe^{+3}}{Fe^{+2} + Fe^{+3}} = \frac{0.947}{1.052} = 0.899$$

and $N_{Fe^{+2}} = 0.101$.

Since for pure iron-oxide, $a_{FeO} = 1$ and $N_{O^{-2}} = 1$, the activity of ferrous oxide in any solution is given by

$$a_{FeO} = \frac{1}{0.899} \times N_{Fe^{+2}} \times N_{O^{-2}}$$

$$= 1.112 \times N_{Fe^{+2}} \times N_{O^{-2}}$$

The application of Temkin's theory to highly basic slags presents no problem for the following reason. In such a slag there exists free oxide ions which can be obtained from the relation, $n_{O^{-2}} = n_{CaO} + n_{MnO} + n_{FeO} + n_{MgO} - 2n_{SiO_2} - 3n_{P_2O_5} - 3n_{Al_2O_3} - n_{Fe_2O_3}$

where, $n_{O}^{=a}$ = the number of free oxide ions per 100 g slag

n_{CaO} etc. represent the number of gm moles of lime, etc. present which will give rise to the same number of gm ions of oxygen,

and n_{SiO_2} etc. represent twice the number of gm moles of silica, which is equal to the gm ions of oxygen consumed to form the $SiO_4^{=4}$ anion and so on. However, P_2O_5 and Al_2O_3 are known to exist as the compounds $4MO.P_2O_5$ and $MO.Al_2O_3$ respectively instead of $3MO.P_2O_5$ and $3MO.Al_2O_3$ in solid slags but the assumption of the ions $P_2O_5^{-4}$ and $Al_2O_4^{-2}$ do not bring in significant error in the calculation of $n_O^{=a}$ since their percentages are very small. Since silica in a highly basic slag exists almost exclusively as SiO_4^{-4} anion, at least a direct proportionality between activity of any constituent in the liquid slag and the ionic fraction product can be found.

As an approach to this problem, Chipman and Chang[101] applied the ionization concept to slags containing lime, magnesia, iron oxide and silica equilibrated with molten iron (i.e. the experimental results of Fetters and Chipman[99]). They assumed the ionic species Ca^{+2}, Mg^{+2}, Fe^{+a}, O^{-a}, SiO_4^{-4} and $Fe_2O_5^{-4}$, and calculated the ionic fractions of Fe^{+a} and O^{-a} on the Temkin Model. While $a_{Fe^{+a}}$ was taken as equal to $N_{Fe^{+a}}$, a value of ν was assigned to oxide ion to account for its deviation from ideality,

That is,

$$a_{FeO} = N_{Fe^{++}} \cdot \nu \cdot N_{O^{--}}$$

The activity of ferrous oxide can be obtained from the oxygen content of the metal and the equilibrium constant for the oxygen equilibrium. Hence ν was calculated for each slag composition. A plot of ν vs $(N_{Ca^{++}} + N_{Mg^{++}})$ showed that it is substantially constant and close to unity within the limits of experimental error. The activity of ferrous oxide is therefore

$$a_{FeO} = N_{Fe^{++}} \times N_{O^{--}}$$

The theory is more difficult to apply to less basic compositions in view of the lack of knowledge of the existence of the ionic species of silica, alumina and phosphorous pentoxide. In order to apply this theory assumptions have been made about the composition of these ions.-

Using the results of Davidson and Bodsworth[97] on the activities of ferrous oxide in melts of the system FeO-CaO-MnO-SiO_2, Mason[100] has found a direct proportionality between the measured activity of ferrous oxide and the ionic product $(n_{Fe^{++}})(n_{O^{--}})$. Although the actual calculation of $n_{O^{--}}$ is not shown, the assumption made regarding the nature of silicate ion seems to suggest that,

$$n_{O^{--}} = n_{FeO} + n_{CaO} + n_{MnO} - n_{SiO_2}$$

SiO_3^{--} ion was assumed rather than SiO_4^{----} ion.

This contention is supported by the possible thermal dissociation of the orthosilicate groups in silicate melts more acid than the orthosilicate composition as suggested by Richardson[100].

That is,

$$2SiO_3^{--} \longrightarrow Si_2O_7^{------} + O^{--}$$

Further dissociation of $Si_2O_7^{------}$ to give rise to SiO_3^{--} is assumed by Masson to account for the observations

$$Si_2O_7^{------} \longrightarrow 2SiO_3^{--} + O^{--}$$

The formation of orthosilicate from silica can therefore be postulated by a sequence of reactions such as:-

$$2SiO_2 \xrightarrow{2(O^{--})} 2SiO_3^{--} \xrightarrow{(O^{--})} Si_2O_7^{------} \xrightarrow{(O^{--})} 2SiO_4^{----}$$

An indirect evidence as to the existence of species other than SiO_3^{--} is obtained from freezing point measurements of Ca_2SiO_4. However, no X-ray evidence exists as to the possibility of existence of SiO_3^{--} ion in solid silicates. Moreover, the activity of ferrous oxide has some low finite value at the metasilicate join (as discussed by Davidson and Bodsworth in the same paper) whereas the diagram of Masson predicts zero value for the activity of ferrous oxide at this composition. It appears that the Temkin line overestimates the more basic slag compositions and underestimates the less basic compositions than the meta silicate join. That is, for more basic compositions $n_{O^{--}}$

is given by,

$$n_{O^{--}} = n_{MnO} + n_{FeO} + n_{CaO} - 2n_{SiO_2}$$

This would partly explain the slight scatter in his diagram. In spite of these remarks the approach merits consideration.

In an attempt to apply Teskin's theory to the present results, a similar assumption was found necessary as regards the nature of existence of the aluminate ion. Calculating on the basis of the usual AlO_3^{-3} ions, it was realised that there are no free oxide ions. However, the existence of $Al_2O_5^{-n}$ ions and SiO_3^{-2} ions (in alumino silicate slags) was tacitly assumed and $N_{O^{--}}$ calculated. The calculations can be illustrated by melt 34 as follows:-

TABLE 32 - CALCULATION OF IONIC FRACTIONS FROM SLAG ANALYSIS

Slag Analysis		Gram Cations Formed	Gram Anions formed (O^{-2} or S^{-2})	Gram Oxide ions consumed	Gram Oxide ions (free)
$(CaO)_b$	42.6				
$(CaO)_{return}$	40.3	$g_{Ca}^{+2} = \frac{40.3}{56.1} = 0.72$	0.72		
CaS	2.955	$g_{Ca}^{+2} = \frac{2.955}{72.14} = 0.0409$	0.0409		
MgO	8.52	$g_{Mg}^{+2} = \frac{8.52}{40.32} = 0.211$	0.211		
$(FeO)_b$	0.835	$g_{Fe}^{+2} = \frac{0.835}{71.85} = 0.01161$	0.01161		
Al_2O_3	43.34			$\frac{43.34}{102} = 0.4225$	
SiO_2	4.25			$\frac{2 \times 4.25}{60} = 0.1416$	

Total oxide ion formed - oxide ions consumed
= 0.72 + 0.211 + 0.01161 - 0.4225 - 0.1416
= 0.3765

$$\therefore \quad N_{Fe}^{+2} = \frac{n_{Fe}^{+2}}{\Sigma \text{cations}} = \frac{0.01161}{0.72 + 0.0400 + 0.213 + 0.01161}$$

$$= \frac{0.01161}{0.99361}$$

$$N_O^{-2} = \frac{n_O^{-2}\ free}{\Sigma \text{anions}} = \frac{n_O^{-2}\ free}{n_O^{-2}\ free + n_S^{-2} + n_{Al_2O_4}^{-2} + n_{SiO_4}^{-4}}$$

$$= \frac{0.3705}{0.3705 + 0.0409 + 0.0225 + 0.0708}$$

$$= \frac{0.3705}{0.5137}$$

$$\therefore \quad N_{Fe}^{+2} \cdot N_O^{-2} = \frac{0.01161}{0.9936} \times \frac{0.3705}{0.5137} = 4.0 \times 10^{-2}$$

The activity of ferrous oxide = 5.275×10^{-2}

Mole fraction of ferrous oxide = 7.80×10^{-2}

The calculated values of $N_{Fe}^{+2} \cdot N_O^{-2}$ are presented in Tables 8 and 10, which show excellent agreement with the activities and mole fractions of ferrous oxide. It will be seen that the values of the product of the ionic fractions are in general lower than the mole fractions and this tendency is significant in slags containing silica.

In Fig. 22, the activity of ferrous oxide has been plotted against the ionic fraction product. The Temkin line, which has a slope of 1.114, is also shown in the figure. A comparison of this Figure with Fig. 14 shows that the scatter of the points about the Temkin line is of the same order or probably slightly better than

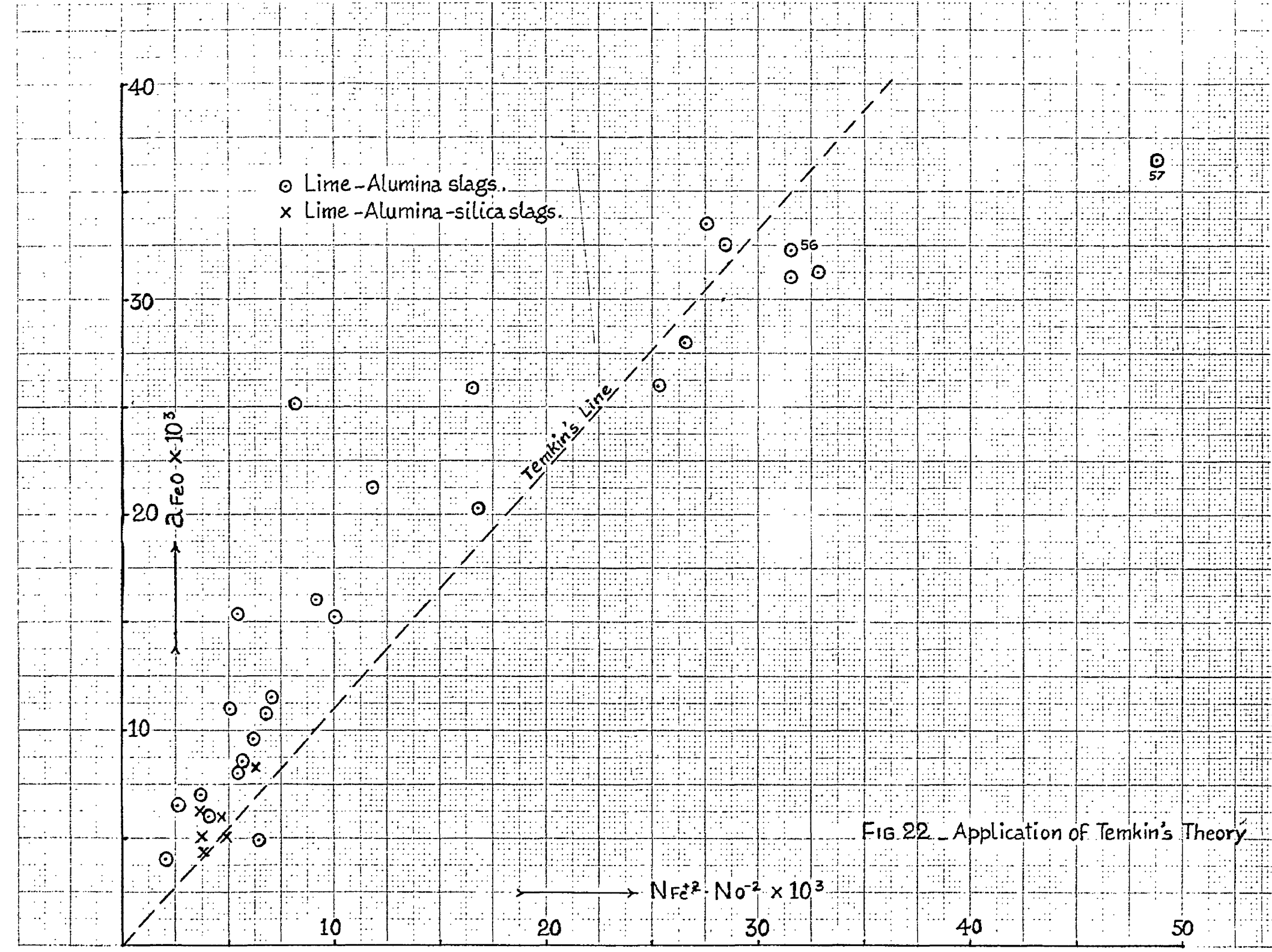


FIG. 22 - Application of Temkin's Theory

the scatter about the Raoultian line. Points marked 56 and 57, again, are those corresponding to the re-analysed values of ferrous oxide. It can be seen that there is reasonable agreement between Temkin's Law and Raoult's Law in the present study. The same observation has been made by Chang and Chipman for higher concentrations (0·5 - 0·85 mole fraction of FeO). Keeping in mind the method by which activity of ferrous oxide has been derived, the application of Temkin's theory to the present results can be considered satisfactory. It appears that the theory can be applied here with as much success as to the results of Chipman and Chang. However, until further information as regards the nature of aluminate ion in liquid slag is available, this treatment should be regarded as empirical only.

A more serious objection to Temkin's theory is the implication that it does not account for the differences in energies of interaction of the various ion pairs. This tends to cause preferential association of ions depending on their size, charge, co-ordination no. etc. This aspect is considered in Section (3).

(3) APPLICATION OF FLOOD'S THEORY

Following Temkin, Flood et al[60] were able to give a cyclic solution treatment to slag-metal equilibria and predict the dependance of the equilibrium quotient on the composition of the slag. This is perhaps the most significant approach in ionic treatment of slag constitution to date. In their model, Flood et al[61] accounted for the energies of interaction of the various ion pairs. For example, since one divalent ion must substitute for two monovalent ions to preserve electro-neutrality and so on, the 'electrically equivalent fraction' of a divalent ion, say calcium, in a slag containing Na^{+}, Ca^{+2} ... cations is given by

$$N'_{Ca^{+2}} = \frac{2n_{Ca^{+2}}}{n_{Na^{+}} + 2n_{Ca^{+2}} + \ldots\ldots}$$

For ions of the same sign and charge, however, the Temkin's ionic fraction and Flood's electrically equivalent fraction are the same.

It was shown that

$$\log K' = \sum_{i} N'_i \log K'_i + \Sigma(\nu)$$

where

K' = the mixed anionic equilibrium quotient, defined in terms of the atomic percent of solute elements in the metal and ionic fractions in the slag, i.e. $K' = \frac{(N_S^{-2})[O]}{(N_O^{-2})[S]}$ for the sulphur equilibrium.

N'_i = the electrically equivalent cation fraction

K'_i = the equilibrium quotient involving the cation i only in the reaction.

and $f(\nu)$ represents the deviation from ideal behaviour of the cations, i.e. the sum of the activity coefficients in all the binary equilibria involving cations. In simple binary systems, $f(\nu) = 0$, but in practice departure from ideal mixing may be expected. Assuming $f(\nu) = 0$, the above equation simplifies to,

$$\log K' = \sum_i^{\prime} N' \log K'_i$$

$$= N'_{Ca} \log K'_{Ca} + N'_{Mg} \log K'_{Mg} + N'_{Fe} \log K'_{Fe} \ldots.$$

Of particular interest in this equation is the influence of the cation on the equilibrium (anionic) quotient K'. Using the data of Winkler and Chipman[26], Flood et al[60] demonstrated the utility of this equation to sulphur equilibrium. It was shown that $\log K'$ is independent of the ionic fraction of calcium, N'_{Ca}[26]. This would suggest that in the above equation,

$$K'_{Ca} = K'_{Mg} = K'_{Fe} \ldots\ldots\ldots$$

Since thermodynamic considerations rule out this possibility, the apparent constancy of K' should only be regarded as a fortuitous occurrence. The scatter obtained in the plot of Winkler and Chipman data is too great to draw any reliable conclusion. It is a pity that the existing experimental data on sulphur equilibrium are inadequate to test Flood's equation. Nevertheless, the calculated and experimental values of K' agree well enough in

excellent agreement with Sosanov and Shiltsov[98].

A modification of the equilibrium quotient has been attempted by Hard[99] accounting for the atomic interaction of solute elements in liquid metal and redefining their concentrations on the more usual Henrian (1 wt %) standard state rather than the unit mole fraction standard state. The modified equilibrium quotient, K^*, defined in this way, is given by

$$K^* = \frac{(f_O^{-n})[a_O]}{(f_S^{-m})[a_S]}$$

where a_O and a_S are the Henrian activities of oxygen and sulphur in the metal, log K^* is given by,

$$\log K^* = \sum_i^i P_i \log K_i^* + f(y)$$

where K_i^* is the modified equilibrium quotient when only cation i is involved in deoxidation. Further, an attempt has been made to show the dependency of K^* on cation fraction, N_{Fe}^{*n}, using data obtained from various sources. Taking the data of Fetters and Chipman[93], Fischer and Spitzer[100], and Winkler and Chipman[95] separately, there appears to be no significant dependency of K^* on N_{Fe}^{*n}. The data of Fetters and Chipman, however, show a slight dependency. Data for wider composition range are required to test the above equation.

The equilibrium quotient for the reaction,

$$O^{-a} + S = S^{-a} + O \quad \ldots\ldots\ldots(15)$$

$$K'_{15} = \frac{(f_S^{-a})[\%O]}{(f_O^{-a})[a_S]}$$

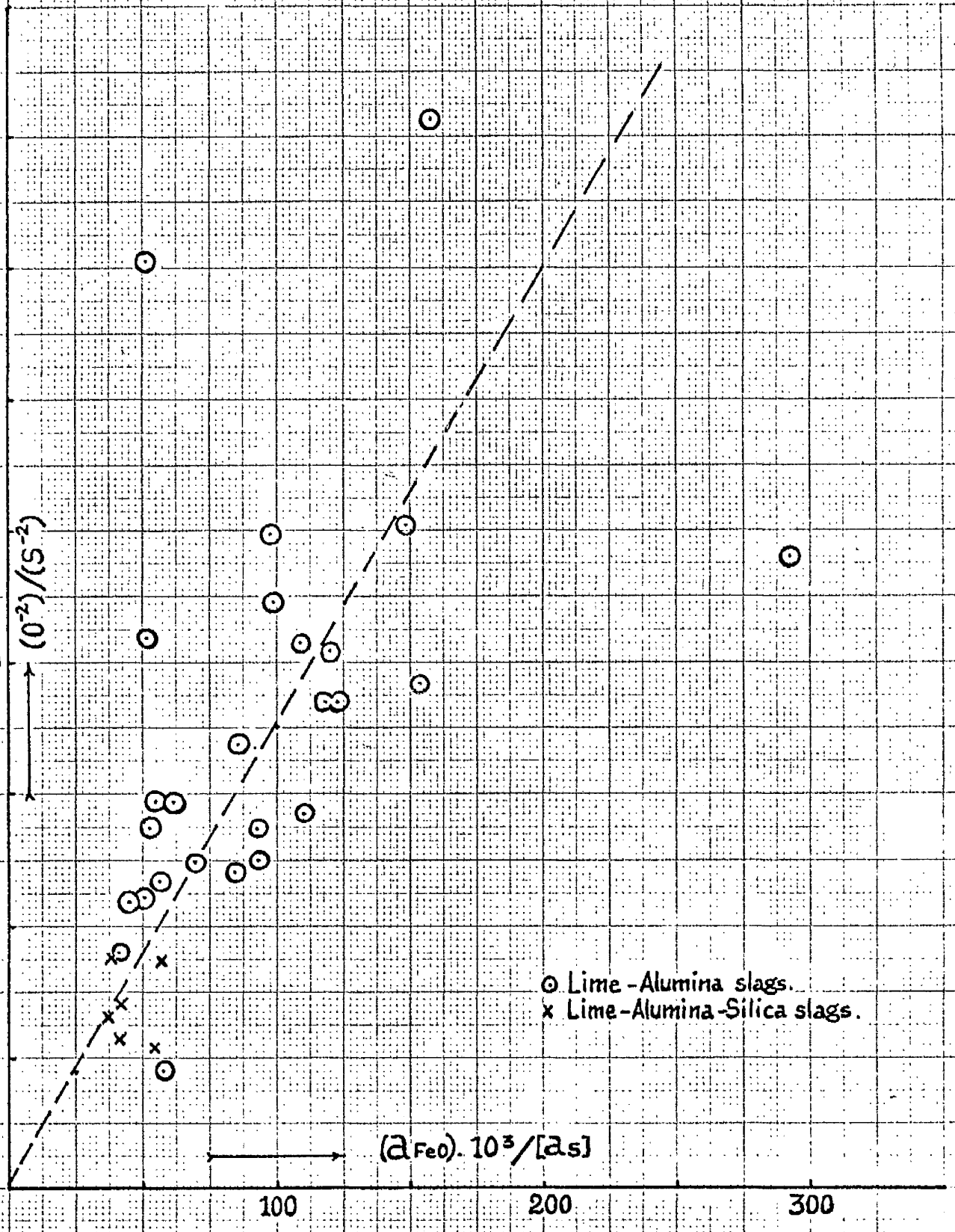


FIG 23 Relation between $(O^{-2})/(S^{-2})$ and $(a_{FeO})/[a_S]$

TABLE 13 - Calculated ratio of oxygen ion to sulphide ion against ratio of activities of ferrous oxide in the slag to sulphur in the metal, the derived equilibrium ratio and composition.

Melt No	$\frac{(N_O^{--})}{(N_S^{--})}$	$\frac{a_{FeO}}{[\%S]} \times 10^0$	log K_{Fe}	N_{Ca} ++	N_{Fe} ++
21	24·1	252·2	-2·6374	0·8475	0·0097
22	22·4	69·8	-3·0768	0·75	0·00864
23	25·22	148·2	-2·9521	0·78	0·00678
24	92	382	-3·0815	0·758	0·03702
25	9·07	41·2	-3·0642	0·823	0·005125
26	12·43	66·5	-2·9809	0·7725	0·00737
27	4·57	58	-2·6171	0·94	0·00528
28	12·18	69·7	-2·8645	0·818	0·00758
34	8·77	57·1	-2·9077	0·79	0·01195
35	7·18	40·1	-2·9767	0·796	0·0115
36	8·9	38·65	-3·0835	0·72	0·01007
37	5·38	54·25	-2·7179	0·832	·01405
38	6·625	97	-2·9743	0·715	0·00964
39	5·725	26·65	-3·0581	0·69	0·01833
42	40·8	157·8	-3·1343	0·712	0·0229
44	18·65	118·7	-2·918	0·742	0·01312
45	11·1	50·5	-3·063	0·7475	0·01195
46	12·62	92·6	-2·8564	0·747	0·01047
47	11·8	56·2	-3·0434	0·6725	0·0154

TABLE 13 (cont'd)

Melt No	$\frac{(N_O^{--})}{(N_S^{--})}$	$\frac{C_{FeO}}{[a_S]} \times 10^6$	log K'_S	N_{Ca}^{++}	N_{Fe}^{++}
48	19.25	158.5	-2.8196	0.681	0.01252
50	21	51.0	-3.3288	0.64	0.0458
51	20.75	100	-3.0000	0.6725	0.0408
52	18.4	123.7	-2.8915	0.704	0.0295
53	14.75	61.3	-3.1029	0.6725	0.03175
54	16.85	85.8	-3.0144	0.686	0.0328
55	13.75	92.5	-2.8934	0.701	0.0267
56	24.95	97.4	-3.1296	0.709	0.0281
57	35.35	80.6	-2.909	0.711	0.0294
58	13.8	52	-3.1491	0.7225	0.035
59	20.48	119.9	-2.9547	0.7275	0.04345
60	11.08	45.3	-3.109	0.7	0.01367
61	14.2	110.2	-2.8312	0.767	0.02765
62	11.76	54.2	-3.1561	0.6863	0.0199

can be derived from the present results from a plot of $\frac{(a_O^{=})}{(a_{O^{=}})}$ vs $\frac{a_{FeO}}{[a_O]}$. The calculations made to determine $\frac{(a_O^{=})}{(a_{O^{=}})}$ are the same as that shown in page 125, assuming alumina to be present exclusively as AlO_2^{-} ion. For example, in melt 59,

$$\frac{(a_O^{=})}{(a_{O^{=}})} = \frac{a_O^{=}}{a_{O^{=}}} = \frac{0{\cdot}59456}{0{\cdot}0383} = 14{\cdot}75$$

and $$\frac{a_{FeO}}{[a_O]} = \frac{25{\cdot}05 \times 10^{-2}}{0{\cdot}4335 \times 0{\cdot}7725} = 61{\cdot}3 \times 10^{-2}.$$

This plot for all the melts is shown in Fig. 23 and the necessary data given in Table 13.

It can be seen that there is wide scatter about the average line drawn whose slope is $0{\cdot}19/K'_{35}$. The scatter, however, must be in part due to the compositional dependence of the derived equilibrium quotient.

A similar plot, $\frac{(wt\ \%\ S)}{[wt\ \%\ S]}$ vs $\frac{a_O^{=}}{[wt\ \%\ O]}$

has been made by Carter[52] in an attempt to establish the mechanism of sulphur partition in the basic open hearth range. This is reproduced in Fig. 24 for comparison. Since (%S) is proportional to $(a_{S^{=}})$ and [wt % S] at low concentrations is proportional to $[a_O]$, a comparison can be made between the plot of Carter and the present plot. It can be seen that the scatter here is slightly worse. A possible explanation for this is found in the calculation of $a_O^{=}$. The calculation of $a_O^{=}$ in a basic open hearth slag causes no appreciable error whereas the value of $a_O^{=}$ here depends

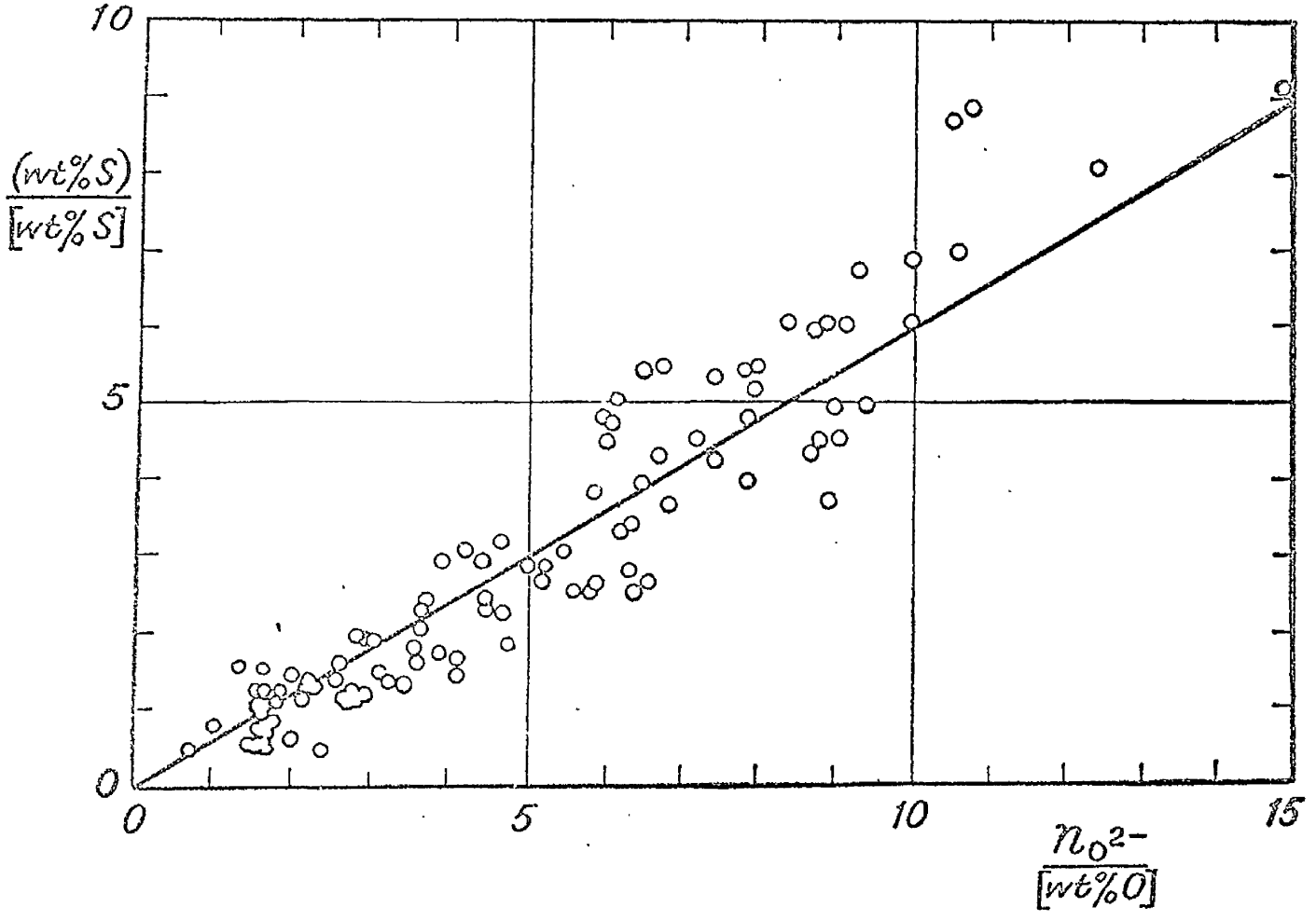


FIG 24 - Linear relation between sulphur and oxygen distribution ratios at about 1600°C[23,48] (after Carter[52])

on the nature of the aluminate ion assumed.

From Fig. 23, the slope of the dotted line is given by $\frac{7.5}{22.5 \times 10^{-3}}$.

Identifying this with $\frac{0.19}{K'_{15}}$, K'_{15} is obtained as

$$K'_{15} = \frac{0.19 \times 22.5 \times 10^{-3}}{7.5} = 1.075 \times 10^{-3} = \underline{0.001075}.$$

This is a very low value for K'_{15} and it indicates that other ionic species of alumina could be present in the slag depending on its composition.

The dependence of K'_{15} on the cationic composition of slag has been examined further. In Figures 25 and 26, log K'_{15} is plotted against $N_{Ca}{}^{++}$ and $N_{Fe}{}^{++}$ respectively, the cation fractions being calculated on the basis of the Temkin model. K'_{15} has been calculated separately for each slag as $0.19 \times \frac{(a_{FeO})}{[a_O^{--}]} / \frac{(O^{--})}{(S^{--})}$.

It can be seen that the plots do not show any dependence of log K'_{15} on $N_{Ca}{}^{++}$ or $N_{Fe}{}^{++}$ and a value of 10^{-3} can be obtained from them for K'_{15}.

It has been seen from the above discussion that the calculation of the equilibrium quotient involves a complete knowledge of the ionic species present in the slag, especially those of alumina. Until this information is obtained, no proper calculation of K'_{15} is possible. It will be interesting, however, to attempt to assess the nature of the aluminate ion assuming Flood's K value of 0.032 at 1600°C. At 1550°C, under the present

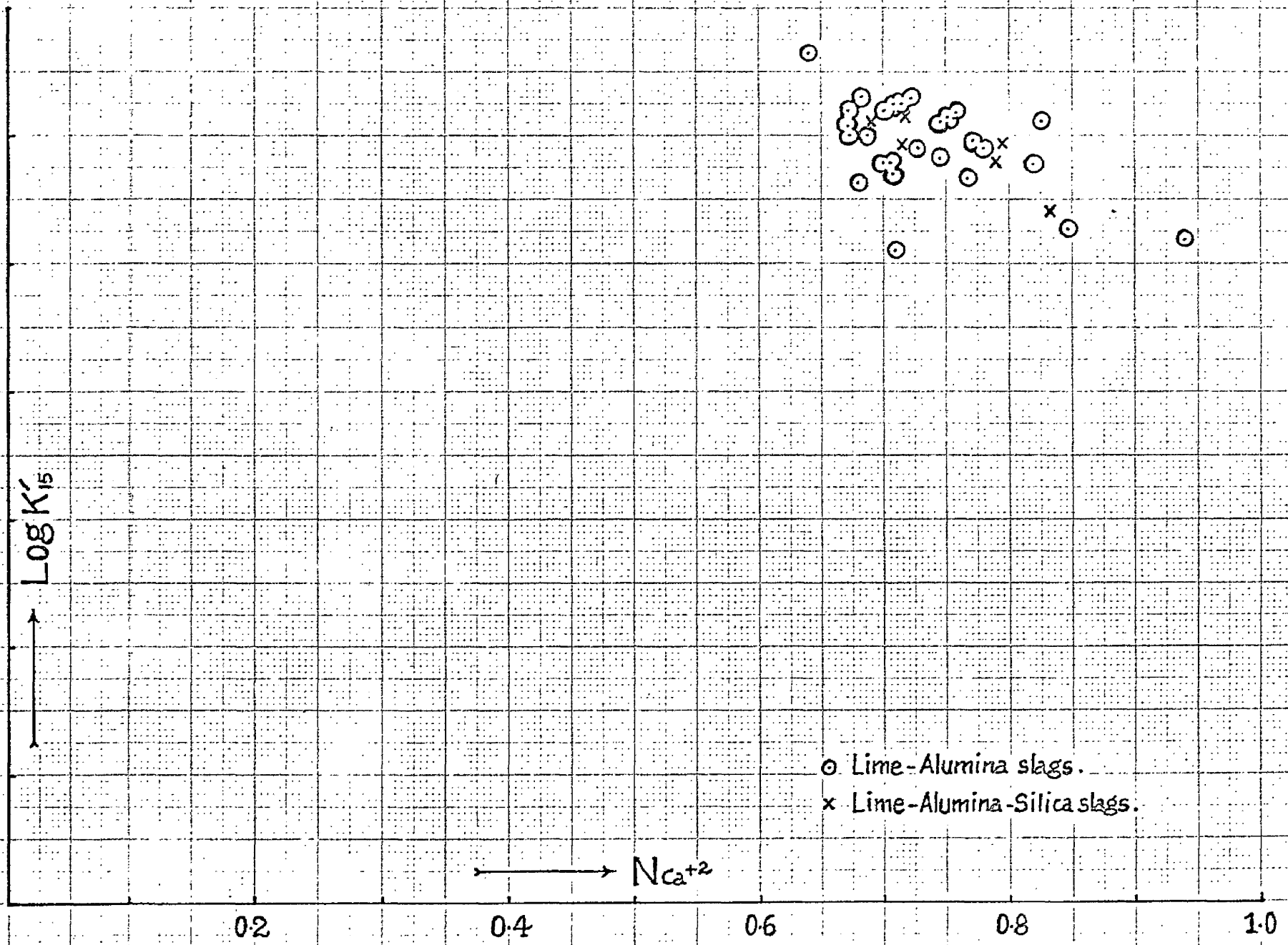


FIG 25 - Dependence of the equilibrium quotient on the ionic fraction of calcium.

$$K'_{15} = \frac{(N_{S^{-2}})[\%O]}{(N_{O^{-2}})[a_S]}$$

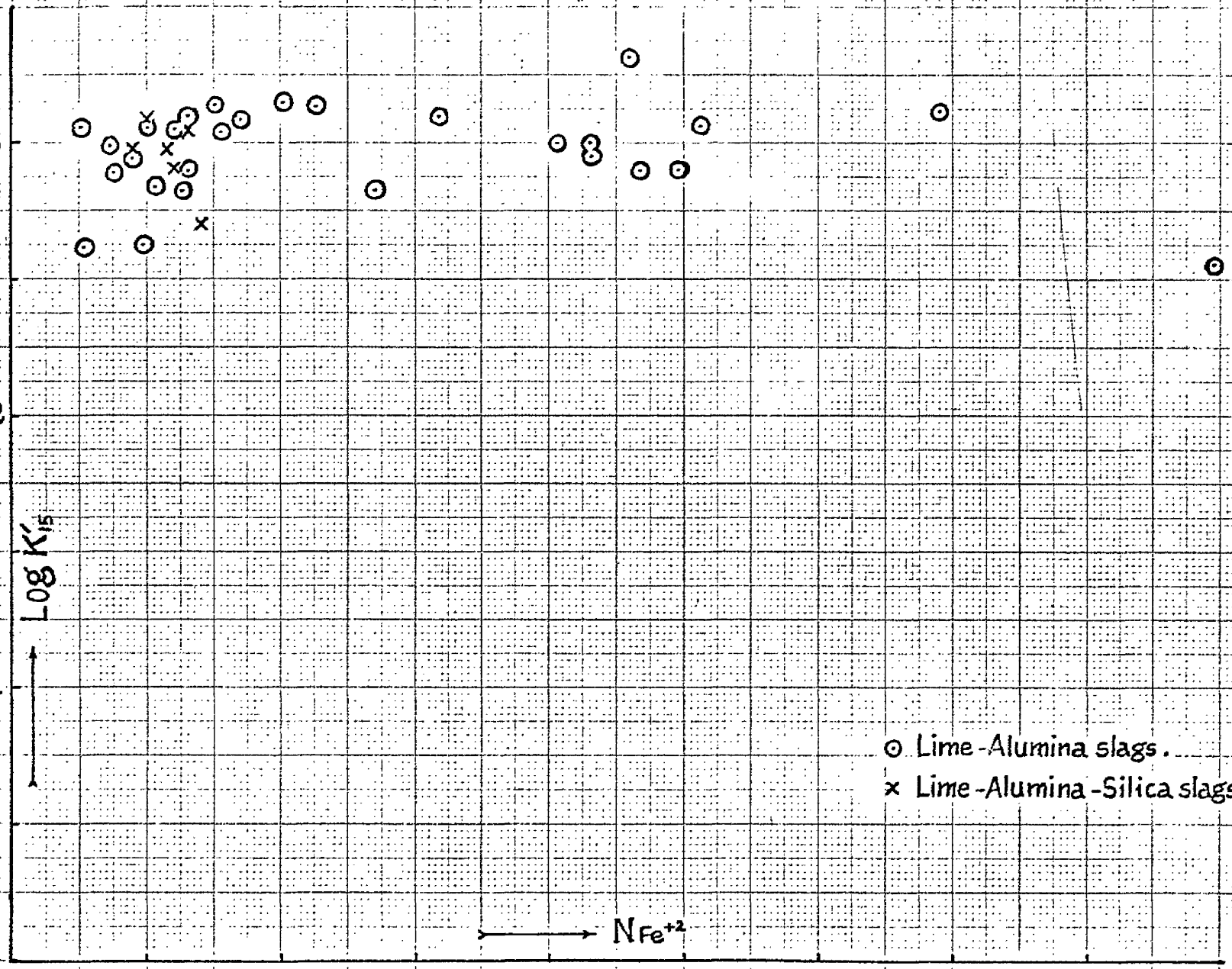


FIG 26 - Dependence of the equilibrium quotient on the ionic fraction of ferrous iron.

$$K'_{15} = \frac{(N_{S^{-2}})[\%O]}{(N_{O^{-2}})[a_S]}$$

experimental conditions, a value of 0·02 can be taken for the equilibrium quotient, $\frac{(a_{O^{-2}})}{(a_{O_2})(a_{Si})} = \frac{[\%O]}{[\%Si]}$. If the form of the aluminate ion at a given slag composition is $AlO_x^{-(2x-6)}$, the problem now is to determine the value of x. This can be illustrated by Run 53.

$$\frac{(a_{O^{-2}})[\%O]}{(a_{O_2})[\%Si]} = 0{\cdot}02$$

$$\text{i.e. } a_{O^{-2}} = \frac{(a_{O^{-2}})[\%O]}{[\%Si] \times 0{\cdot}02}$$

$$= \frac{(a_{O^{-2}}) \times 0{\cdot}19 \times a_{FeO}}{0{\cdot}02 \times [\%Si]} \quad \text{since} \quad \frac{[\%O]}{a_{FeO}} = 0{\cdot}19 \text{ at } 1550^{\circ}C$$

$$= \frac{(a_{O^{-2}}) \times 0{\cdot}19 \times a_{FeO} \times [\%Al]}{0{\cdot}02 \times [a_{Al}]}$$

$$= \frac{9{\cdot}5 \times (a_{O^{-2}}) \times [\%Al] \times a_{FeO}}{[a_{Al}]}$$

But $[\%Al] = 0{\cdot}0725$, $\frac{a_{FeO}}{[a_{Al}]} = 61{\cdot}3 \times 10^{-3}$ and $a_{O^{-2}} = \frac{0{\cdot}0362}{1{\cdot}0247}$,

Substituting $a_{O^{-2}} = 9{\cdot}5 \times \frac{0{\cdot}0362}{1{\cdot}0247} \times 0{\cdot}0725 \times 61{\cdot}3 \times 10^{-3}$

$= 0{\cdot}02$.

Hence, $a_{O^{-2}} = 0{\cdot}02 \times 1{\cdot}03475 = 0{\cdot}0205 =$ free oxide ions.

Since total oxide ions = oxide ions consumed by aluminate + free oxide ions

oxide ions consumed by alumina = 0·0805 − 0·0205

$= 0{\cdot}060$

Table 14 Calculated oxide ion fraction and ratio of oxygen to aluminium in the aluminate ion versus slag composition

Melt No.	$N_{O^{=}}$ (calculated from Flood's K)	Ratio of oxygen to aluminium [i.e. $\frac{x}{2}$ where x is involved in the ion $Al_2O_x^{-(2x-6)}$]	% Al_2O_3 (calculated on CaS free basis)	N Al_2O_3 (calculated on CaS free basis
21	0·0698	2·73	41·7	0·274
22	0·0199	2·465	50·1	0·387
23	0·0336	2·775	45·25	0·274
24	0·0346	2·825	49·1	0·344
25	0·019	2·34	53	0·368
26	0·0258	2·51	46·65	0·3255
27	0·0566	2·533	43·5	0·289
20	0·0345	2·575	46·5	0·309
34	0·0229	2·4	44·4	0·296
35	0·01566	2·285	48	0·325
36	0·01342	2·32	46·1	0·321
37	0·0397	2·52	41·1	0·271
38	0·01945	2·42	44·7	0·293
39	0·01361	2·33	47·1	0·311
42	0·0193	2·56	47·5	0·316
44	0·0348	2·7	43·8	0·2955
45	0·0197	2·45	50	0·341
46	0·0432	2·82	43·7	0·266

Table 14 (cont'd)

Melt No.	$N_{O^{=}}$ (calculated from Flood's K)	Ratio of oxygen to aluminium [i.e. $Al_2O_x^{-(2x-6)}$ where x is involved in the ion]	%Al_2O_3 (calculated on CaO free basis)	%Al_2O_3 (calculated on CaS free basis
47	0·0844	2·65	45·8	0·267
48	0·06575	2·77	42·65	0·2735
50	0·0125	2·65	46	0·268
51	0·034	2·65	41·3	0·264
52	0·0415	3·025	37·6	0·239
53	0·02	2·57	47·6	0·3165
54	0·0284	2·79	42·5	0·274
55	0·0428	2·575	36·5	0·244
56	0·0225	2·9	41·5	0·268
57	0·00931	3·31	39	0·2355
58	0·02645	2·445	50·5	0·341
59	0·0331	2·765	41·9	0·273
60	0·0159	2·52	48·85	0·325
61	0·04365	2·83	41·6	0·272
62	0·0171	2·51	46·9	0·326

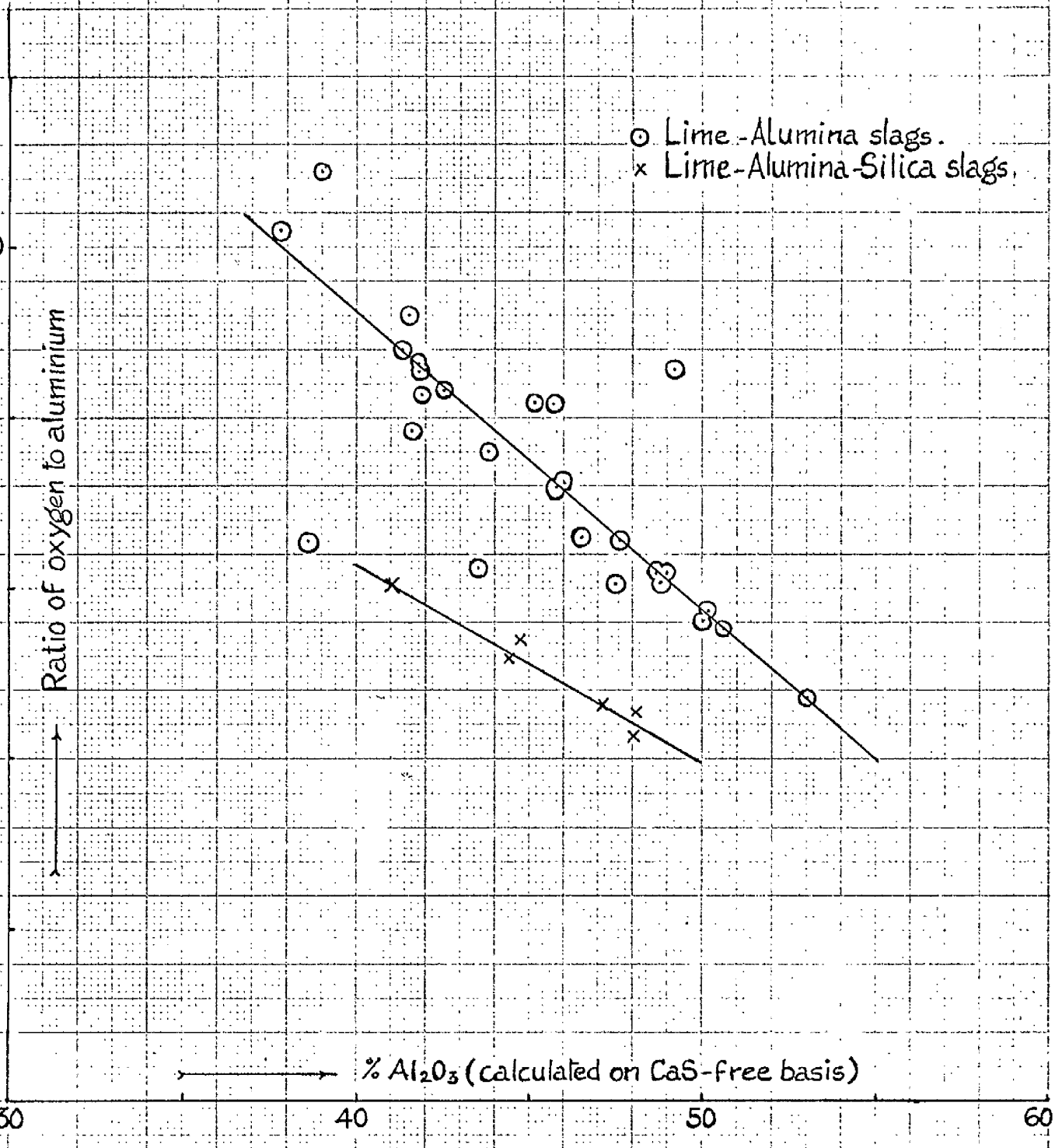


FIG 27 _ Effect of composition on the ratio of oxygen to aluminium in the aluminate ion

Hence

$$0.454\ Al_2O_3 + 0.908\ O^{--} = 0.454\ Al_2O_x \qquad (2x = 6)$$

from which

$$x = \frac{0.454 \times 3 + 0.908}{0.454} = 5.00$$

The general formula to find x will therefore be,

$$x = \frac{3n_{Al_2O_3} + \text{total oxide ions} - \text{free } n_{O^{--}}}{n_{Al_2O_3}}$$

and for lime-alumina-silica slags

$$x = \frac{3n_{Al_2O_3} + \text{total oxide ions} - 2n_{SiO_2} - \text{free } n_{O^{--}}}{n_{Al_2O_3}}$$

x thus refers to the ratio of oxygen to aluminium ; $n_{Al_2O_3}$ or n_{SiO_2} refers to mols per 100 g of slag.

Values of oxygen to aluminium ratio calculated in this way for the various melts are tabulated against $\%Al_2O_3$ and mole fraction of alumina (Table 14) and plotted against $\%\ Al_2O_3$ or mole fraction of alumina (Figs. 27 and 28). It can be seen that the points can be represented approximately by two straight lines, one representing lime-alumina slags and the other lime-alumina-silica slags. As x = 3 at 100% Al_2O_3, the straight line should curve at higher percentages of alumina to satisfy this condition for lime-alumina slags.

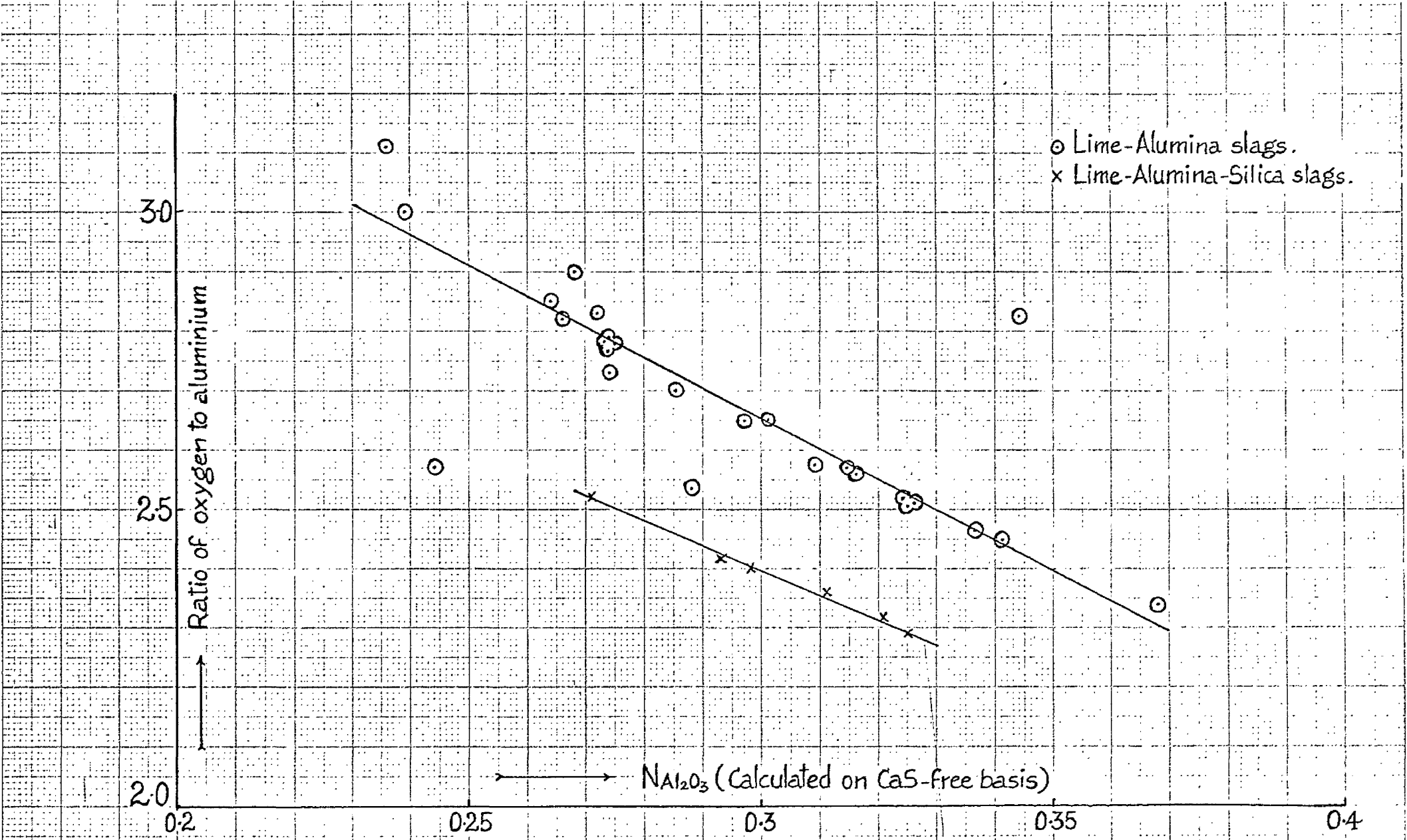
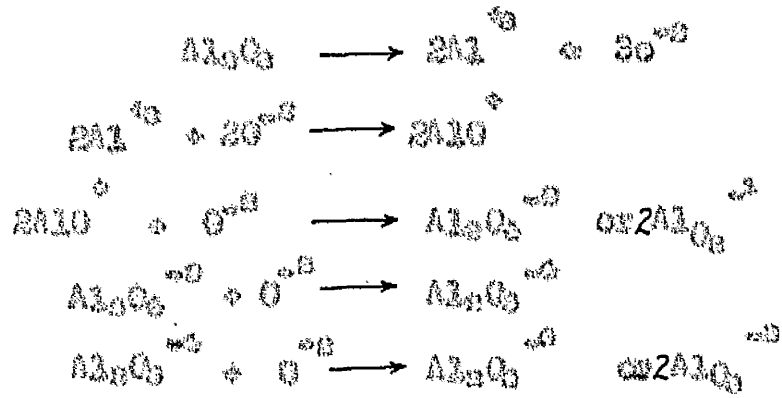


FIG 28_Effect of composition on the ratio of oxygen to aluminium in the aluminate ion

Hence it appears that the aluminate ion in $CaO-Al_2O_3$ slags (containing MgO and FeO) would probably consist of $Al_2O_3^{-2}$ ion at about 60% Al_2O_3. As the basicity is increased, this changes to $Al_2O_3^{-4}$ and $Al_2O_3^{-6}$ ions at about 40 and 30% Al_2O_3 respectively. In lime-alumina-silica slags (containing MgO and FeO) used in this work $Al_2O_3^{-2}$ ion appears to exist at about 57% alumina and the $Al_2O_3^{-4}$ ion is stable at about 42% alumina. It may be noted that x is a measure of the distribution of oxygen atom between two aluminium atom and it does not indicate the different species that are likely to be present at a given slag composition. It is quite possible that a mixture of species of aluminate ion could exist at a given slag composition.

The effect of silica in lime-alumina slags is again of interest. Addition of about 4-5% silica to lime-alumina slags lowers the number of oxygen bound to aluminate ion. This can be explained as being due to the strengthening of the electron field when silicon with four positive charges replaces aluminium. The net result is therefore that lesser number of oxygen atoms are bound to aluminium. This accounts for the greater acidic property of silica compared to alumina. In other words, silica is more powerful in reducing basicity and hence in imparing desulphurization compared to alumina. This has been noted earlier.

The following discussion seems for alumina is therefore proposed to fit in the experimental observations.-


$Al_2O_3 \longrightarrow 2Al^{+3} + 3O^{-2}$
$2Al^{+3} + 2O^{-2} \longrightarrow 2AlO^{+}$
$2AlO^{+} + O^{-2} \longrightarrow Al_2O_3^{-2}$ or $2Al_{O_3}^{-2}$
$Al_2O_3^{-2} + O^{-2} \longrightarrow Al_4O_5^{-4}$
$Al_4O_5^{-4} + O^{-2} \longrightarrow Al_6O_7^{-6}$ or $2Al_{O_3}^{-2}$

and so on.

CHAPTER VI

CONCLUSION

CONCLUSION

(1) General Discussion of Experimental Results.-

In slag-metal equilibrium studies of sulphur, true lime activity values have not been arrived at in view of the lack of knowledge about the variation of activity coefficient of calcium sulphide with composition. However, as a result of gas-slag work in melts saturated with calcium sulphide, lime activity values in lime-alumina at 1600°C lime-silica at 1600°C and to a certain extent lime-alumina-silica at 1600°C melts are available. However, in gas-slag work, for melts not saturated with calcium sulphide, lime activity values can be arrived at with reasonable extrapolation.

It has been shown that distribution experiments in magnesia crucibles are preferable to carbon crucibles in that the ferrous oxide content of the slag could be varied and subsequently determined with greater accuracy than in the case of carbon crucibles. In blast-furnace slags or slags equilibrated in carbon crucibles, ferrous oxide analysis is extremely unsatisfactory for two reasons. Firstly, one faces the problem of separating the dispersed iron particles from the slag. Secondly, the analytical accuracy is low in view of the low iron oxide contents of the slag. The second difficulty could however be circumvented carrying out iron oxide analysis by

spectrophotometry. The first difficulty was to a certain extent overcome by Rabeh and Chipman[49] with the use of a Fronts isodynamic separator and their second analysis was of the same order as the calculated activity of ferrous oxide in the slag in equilibrium with carbon saturated iron at 1500°C. Other advantages of magnesia crucibles over carbon crucibles for slag-metal equilibrium studies of sulphur have been dealt with earlier.

The main result which emerges from the present work is that the activity of iron oxide at low concentrations in the slag is approximately equal to the mole fraction over the range of composition investigated. This appears to be true for complex slags in the region 0·55 - 0·75 mole fraction of CaO + MnO + MgO from the diagram of Tankogan and Pearson (Fig. 19).

The application of ionic theories of slag constitution has stimulated thought in terms of the nature of the aluminate ion in the liquid slag. It is indeed surprising that calculations made on the assumption of the existence of $Al_2O_6^{-6}$ ion fits in reasonably well with the activity - ionic fraction product relationship for ferrous oxide in line with Temkin's concept. This fit is as good as Knould's line fitting the activity - mole fraction relationship for iron oxide. The only dubious feature of this treatment appears to be the basic assumption involved, for there is no experimental evidence as to the nature of existence of $Al_2O_6^{-6}$ ion at the slag-compositions

studied. It may be more probable that equilibrium between two or more species of aluminate ion could exist at any particular composition. However, comparing the a_{FeO}, N_{FeO}, $N_{Fe^{++}} \times N_{O^{--}}$ values given in Tables 8 and 10 and Figs. 14 and 22, one is likely to be biased by Temkin's theory. Moreover, at low concentrations of ferrous oxide in the slag, $\gamma_{Fe^{++}} = \gamma_{O^{--}} = 1$, and hence providing justification to Temkin's theory. It should be pointed out here that calculation of ionic fraction of oxide ion, $N_{O^{--}}$, on the basis of existence of $Al_2O_3^{--}$ ion does not fit in the Temkin's line. In a few slags it has been noted that no free oxide ions are available to calculate $N_{O^{--}}$ i.e. $n_{O^{--}}$ is a negative quantity. $Al_2O_3^{--}$ ion again is out of question for the same reason.

In an attempt to apply Flood's theory to the present results, the nature of the existence of the aluminate ion at any particular composition of slag, lime-alumina or lime-alumina-silica, has been pointed out. This is in line with our knowledge regarding the acidic properties of silica and amphoteric properties of alumina. Further treatment of slag constitution in terms of the equilibrium constants for the ionic species of aluminate ion seems to be possible provided we have a complete knowledge of the existence of these ionic species.

(2) APPLICATION OF THE RESULTS.

The application of the present results is considered under two sections, which might, under certain circumstances be of some value. These are:-

(a) Determination of sulphide capacity of simple and more complex slags.

(b) Application to blast furnace practice.

(a) Determination of sulphide capacity of simple and more complex slags.

It has been seen that true iron activity values are difficult to obtain by slag-metal or gas-slag equilibrium measurements of sulphur partition and so the sulphide capacity of the slag which is proportional to $a_{O^{--}} / \gamma_{O^{--}}$ can be used at the present moment with some reservation to characterize the slag with respect to its desulphurizing power. Accumulation of sulphide capacity data of simple and more complex slags of the blast furnace and open hearth types should thus be a useful guide to the iron or steel producer until their true oxide ion activity values are available.

It was shown earlier that the sulphide capacity of the slag is related to the iron-oxide activity by means of the relation,

$$C_{FeO} = 44{\cdot}15 \times \frac{a_O}{\frac{(\%S)}{[a_S]}}$$

$$\therefore \quad a_O = \frac{C_{FeO}}{44{\cdot}15} \times \frac{(\%S)}{[a_S]}$$

$$= 0{\cdot}0227 \times a_{FeO} \times \frac{(\%S)}{[a_S]}$$

Thus the sulphide capacity of the slag can be derived from slag-metal sulphur partition. This necessitates, however, a knowledge of the activity of the 'ferrous oxide' in the slag. In slags where the activity-composition relationship for iron oxide have been well-established, the calculation of sulphide capacity presents no problem. In cases where no information is available about the activity of ferrous oxide in the slag Raoultian behaviour can be assumed and the sulphide capacity so computed should be regarded with some reservation.

This should be a valuable tool in accumulating sulphide capacity data of a variety of slags and can be applied to cases where difficulty is encountered in obtaining sulphide capacity from gas-slag work due to volatilization of one or more of the slag constituents[27] or "creeping out" of the slag from the metal crucible.[18] This method has the obvious limitation that the crucible introduces an additional component in the system being studied.

(b) Application to blast furnace practice.

Application of the results to blast furnace practice is severely limited for many reasons. In the first place, blast furnace slags are more complex than the synthetic slags studied here. In the second place, evidence exists to show that sulphur equilibrium is not attained in the blast furnace[106], although considerable desulphurization can be obtained at the low oxygen potentials prevailing in the furnace.

Thirdly, there is simultaneous existence of equilibrium between three or four phases. And finally, the slags here contain greater amounts of iron oxide than are encountered in the blast furnace. However, little reliance should be placed on the iron oxide analyses of blast furnace slags in view of the entrapped iron particles.

The equilibrium desulphurization ratios may be compared with those obtained in practice. Data from two blast furnace plants have been collected and the analysis of pig iron and slag are presented in Tables 15 and 16. Each data for Plant (1) refers to weekly average and for Plant (2) refers to two weeks' average. These are considered more reliable than daily analyses. $\frac{(\%S)}{[\%S]}$ and Hall's ratio for each of the data have been calculated in the usual way. The sulphide capacity of the slag has been computed in the last column using Fig. 16B.

In Fig. 16A, the distribution ratios so obtained are plotted against sulphide capacity of the slag. The red points refer to Plant (1) and green points refer to plant (2) and an average line has been drawn through the points. (This plot is preferable to the conventional plot of $(\%S)/[\%S]$ vs basicity in view of case of extrapolation). The dotted line in the figure refers to $p_{CO} = 1$ atmosphere and line A refers to $p_{CO} = 2$ atmosphere. The pressure

TABLE 15 - DATA FOR PLANT I

No.	Pig Iron					Slag										
	% C	% Si	% Mn	% S	% P	% CaO	% MgO	% FeO	% MnO	% Al_2O_3	% SiO_2	% S	$\frac{(\%S)}{[\%S]}$	[Fe]	$\frac{(\%S)}{[C_S]}$	Sell's Ratio	$C_S = 10^{\circ}$
1	4·4	0·73	1·28	0·031	0·37	46·4	4·9	0·45	0·9	13·4	33·5	1·39	44·9	4·66	2·6	1·46	28·6
2	4·25	0·69	1·39	0·027	0·40	48·5	2·8	0·58	0·98	13·3	33·4	1·48	54·9	4·17	13·17	1·49	34
3.	4·27	0·65	1·3	0·034	0·41	47·5	2·6	0·58	1·00	14·3	33·5	1·41	41·5	4·27	9·73	1·45	28·5
4.	4·34	0·7	1·46	0·035	0·46	46·2	3·43	0·63	1·45	13·3	34·5	1·32	37·7	4·27	8·84	1·395	23·6
5.	4·13	0·67	1·17	0·035	0·41	46·1	3·2	0·31	1·27	14·1	34·7	1·28	36·6	3·89	9·41	1·375	21·8
6.	4·04	0·75	1·21	0·046	0·73	42·8	4·3	0·65	1·36	15·5	33·7	1·2	26·1	4·37	5·975	1·32	18
7.	3·87	1·84	0·91	0·036	0·62	40·1	2·55	0·39	0·55	24	32	1·13	32·8	4·9	6·7	1·22	13
8.	4·16	0·82	0·82	0·04	0·33	43·4	3·8	0·17	1·22	16·6	34·8	1·26	31·5	4·47	7·05	1·3	17
9.	4·04	0·83	1	0·032	0·48	44·2	3·5	0·23	0·77	15·6	35·4	1·21	37·9	4·22	8·98	1·29	16·5
10.	4·29	0·91	0·92	0·028	0·24	47·6	3·5	0·19	0·91	11·8	35·6	1·32	47·2	4·57	10·3	1·4	23·6

TABLE 15 - DATA FOR PLANT 2

No.	Pig Iron %				Slag %											$C_s \times 10^3$
	Si	Mn	P	S	Fe	CaO	MgO	Al_2O_3	SiO_2	S	$\frac{(S)}{[S]}$	(Fe)	$\frac{(S)}{[S]}$	Ball-Rankin		
1.	3.9	0.77	1.09	0.044	0.85	42	2.65	0.71	1.74	17.35	34.29	0.82	20.9	4.12	4.86	1.269	14.4
2.	4.01	1	1.19	0.08	0.85	42.8	2.86	0.52	1.43	17.7	34.4	0.93	24.75	4.68	5.28	1.235	13.8
3.	4.05	0.93	1.25	0.082	0.81	40.5	4.42	0.54	1.56	18	33.8	0.98	29	4.37	6.35	1.249	14
4.	4.12	0.97	1.19	0.081	0.73	38.1	6.36	0.47	1.28	19.1	33.7	1.01	32.6	4.73	6.89	1.21	12.6
5.	4.02	0.89	0.93	0.04	0.9	37.6	6.28	0.6	1.08	19.7	33.9	0.91	22.7	4.82	5.02	1.19	11.8
6.	4.02	0.72	0.9	0.06	0.83	38.0	7.01	0.47	1.06	19	33.4	0.9	22.6	4.22	5.34	1.23	12.6
7.	4.01	0.96	0.95	0.035	0.87	37.52	6.6	0.78	1.2	19.5	33.9	0.97	26.9	4.52	5.95	1.21	12.6

of carbon monoxide corresponding to line B is given by x in the relation,

$$C_g = \frac{(\%S)}{[\%S]} \times x \times 0{\cdot}7302 \times 10^{-3}$$

From the figure, $C_g = 0{\cdot}275 \times 10^{-3}$ at $(\%S)/[\%S] = 12.$

Substituting, $0{\cdot}275 \times 10^{-3} = 12 \times x \times 0{\cdot}7302 \times 10^{-3}$

$$\therefore x = 3{\cdot}15^{*}$$

The partial pressure of carbon monoxide corresponding to line B is 3·15 atmospheres and this refers to an equilibrium condition. The actual partial pressure of carbon monoxide in the hearth and bosh region of the furnace is about 0·5 atmosphere for normal operation. However, the carbon-monoxide pressure at the slag-metal interface is about 2 atmospheres as measured by the silicon equilibrium. The lower partial pressure of carbon monoxide in practice compared to the equilibrium value implies greater oxygen potential or higher iron oxide content of the slag. Comparing the iron oxide analyses, also presented in Tables 15 and 16, they are indeed higher than the equilibrium value. However, as mentioned earlier, these are not very reliable.

It can also be seen from Fig. 16A, that the slope of the dotted line is about thrice as much as the slope of line B showing that at constant sulphide capacity equilibrium distribution is about three times the distribution ratio obtained in practice. This shows that sulphur equilibrium is not attained in practice.

The reason for the non-attainment of sulphur equilibrium in the blast furnace may now be briefly considered. Referring to Fig. 2, page 60, it can be seen that the transfer of sulphur from metal to slag is retarded by any one or both of the following factors.

(a) the slow reduction of silica by carbon (which retards the oxidation of silicon from the metal). This can take place in two steps[107] as follows.

$$SiO_2 + 2Fe = \underline{Si} + 2FeO$$

$$2FeO + 2C = 2Fe + 2CO$$

so that the overall reaction is

$$SiO_2 + 2C = \underline{Si} + 2CO$$

(b) the sluggishness of the carbon-oxygen reaction (which retards the transfer of oxygen to the metal).

Of these two factors reaction (a) is more probable, because it has been found that silicon addition to iron accelerated the transfer of sulphur from metal to slag[100] and bubbling carbon monoxide through the bath did not have any significant effect on sulphur transfer from metal to slag[109]. However, in view of the extremely low oxygen concentrations in high silicon iron saturated with carbon, reaction (b) is not completely precluded. The slowness of silica reduction is believed to be mainly due to the high heat of activation required for breaking the Si–O bond[100].

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